

A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DEGRADATION OF SOME POLYELECTROLYTES

BY

MUHAMMAD ZULFIQAR

SUPERVISOR: DR. I.C. McNEILL

Chemistry Department,
University of Glasgow.
October, 1975.

ProQuest Number: 13803963

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 13803963

Published by ProQuest LLC (2018). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

PREFACE

The work described in this thesis was carried out during the period October 1971 to September 1974 at the University of Glasgow, in the Department of Physical Chemistry, which is under the supervision of Professor G.A. Sim.

My thanks are due to my colleagues in the Macromolecular Chemistry group for invaluable assistance and discussion, and to various members of the technical staff of the Chemistry Department, in particular, Mr. J. Gorman and Mrs. F. Lawrie.

Finally, I should like to thank my supervisor, Dr. I.C. McNeill, for suggesting the topic of this thesis, and for his advice and constant encouragement throughout this work.

SUMMARY

All naturally occurring polyelectrolytes are found in an aqueous environment and this feature directed most of the chemical research in this field towards an understanding of polyelectrolyte behaviour in aqueous solution. The very rapid and steady progress in the field of synthetic electrolyte applications in industry has naturally stimulated further interest in the problems of synthesis and thermal stability of this type of polymer.

A brief definition of polyelectrolytes, their classification, and a discussion of tacticity and cation binding in these materials is presented in Chapter 1. The introductory chapter also reviews briefly the relationships between the chemical structure and thermal stability of vinyl polymers.

Chapter 2 summarises the apparatus and experimental techniques employed in the present study. The first part deals with the thermal analysis techniques and the second section describes the techniques used to identify the degradation products both qualitatively and quantitatively.

Monomer preparation, polymerization, and characterization of monomers and polymers is considered in detail in Chapter 3. A brief account of thermal stability of monomers is also included in this chapter.

The thermal degradation of alkali metal salts of polymethacrylic acid is discussed in detail in Chapter 4. The decomposition of these homopolymers is shown to involve depolymerization accompanied by the formation of metal carbonate and cyclic ketones. A mechanism of thermal degradation of the salts of polymethacrylic acid is postulated based on the results obtained.

Chapter 5 details the thermal decomposition of divalent metal salts of polymethacrylic acid, which provides further support for the mechanism proposed in Chapter 4.

In Chapter 6 studies of the thermal degradation of zinc polymethacrylate are reported. The nature of the volatile products and structural changes which can occur during decomposition suggest a similar pattern of degradation to other salts. The maximum rate of volatilization of zinc polymethacrylate is shown to occur at lower temperature than those of other divalent metal salts.

The thermal behaviour of ammonium polymethacrylate is examined in Chapter 7. Thermal decomposition is shown to result in a cyclization reaction between adjacent monomer units before fragmentation to volatile products. Comparisons are made between ammonium polymethacrylate, polymethacrylamide and polymethacrylic acid degradation, hence thermal decomposition of the latter homopolymers is also considered in Chapter 7.

CONTENTS

| | <u>Page</u> |
|---|-------------|
| <u>Chapter 1</u> | |
| Introduction | 1 |
| Polyelectrolyte | 1 |
| Classification | 2 |
| Cation binding in polyelectrolyte | 4 |
| Tacticity | 5 |
| Degradation of polymers | 6 |
| Classification of reactions | 8 |
| Chain scission or depolymerization | 9 |
| Effect of polymer structure on depolymerization | 13 |
| Substituent reactions | 14 |
| General considerations | 19 |
| Previous work on salts of poly (methacrylic acid) | 20 |
| Aim of this work | 21 |
| <u>Chapter 2</u> | |
| Apparatus and experimental techniques | 22 |
| Thermal volatilization analysis | 22 |
| Thermogravimetric analysis | 30 |
| Differential thermal analysis | 31 |
| Infra red spectroscopy | 31 |
| Gas chromatography | 42 |

| | <u>Page</u> |
|---|-------------|
| <u>Chapter 3</u> | |
| Monomer and polymer preparation | 47 |
| Introduction | 47 |
| Preparation of the monomers | 49 |
| Characterization of monomers | 52 |
| Polymerization | 62 |
| Polymer characterization | 71 |
| Thermal stability data of monomers | 73 |
| Product analysis | 84 |
| <u>Chapter 4</u> | |
| Thermal degradation of alkali metal salts of poly (methacrylic acid) | 90 |
| Introduction | 90 |
| Thermal volatilization analysis | 98 |
| Thermogravimetric analysis | 104 |
| Analysis of volatiles | 110 |
| Infra red analysis of volatiles | 110 |
| Liquid products analysis by GLC | 122 |
| Residue analysis | 129 |
| Analysis of the cold-ring fraction | 133 |
| Structural changes during degradation | 139 |
| Proposed reaction mechanism in alkali metal- polymethacrylates | 143 |

Chapter 5

| | |
|--|-----|
| Thermal degradation of alkaline earth metal salts of poly(methacrylic acid) | 147 |
| Introduction | 147 |
| Thermal volatilization analysis | 153 |
| Thermogravimetric analysis | 161 |
| Differential thermal analysis | 167 |
| Product analysis | 168 |
| IR analysis of gaseous volatiles | 168 |
| Gas chromatography of liquid products | 174 |
| Cold-ring fraction analysis | 179 |
| Residue analysis | 181 |
| Structural changes during degradation | 184 |
| Discussion | 188 |

Chapter 6

| | |
|---|-----|
| Thermal degradation of zinc polymethacrylate | 192 |
| Results and discussion | 192 |
| Thermal volatilization | 192 |
| Thermogravimetry | 195 |
| Differential thermal analysis | 197 |
| Product analysis | 197 |
| Structural changes during degradation | 203 |
| Comparison of ZnPMA degradation with those of other divalent salts | 206 |

| <u>Chapter 7</u> | <u>Page</u> |
|---|-------------|
| Introduction | 207 |
| Experimental | 209 |
| Determination of nitrogen in PMAM and NH_4PMA | 210 |
| Thermal volatilization analysis | 213 |
| Thermogravimetric analysis | 219 |
| Differential scanning calorimetry | 226 |
| Product analysis | 228 |
| Structural changes during decomposition | 238 |
| Proposed mechanism | 243 |
| <u>Chapter 8</u> | |
| General conclusions | 248 |
| <u>Appendix</u> | |
| <u>References</u> | |

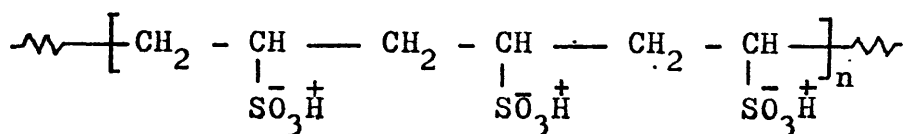
CHAPTER ONE

INTRODUCTION

POLYELECTROLYTE

A polyelectrolyte may be defined as any polymeric substance in which the monomeric units of constituent macromolecules possess ionizable groups.

Poly(ethylene sulfonic acid) is a typical synthetic polyelectrolyte. This substance may be regarded as a polyethylene derivative which contains a highly ionizing sulfonic acid group on every alternate carbon atom of the macromolecular chain:-



In contrast to a simple electrolyte, sodium chloride, in which the sizes of the oppositely charged ions are similar, a polyelectrolyte is always composed of a macroion in which the charged groups are inter connected by chemical bonds, together with an equivalent number of small oppositely charged counterions.

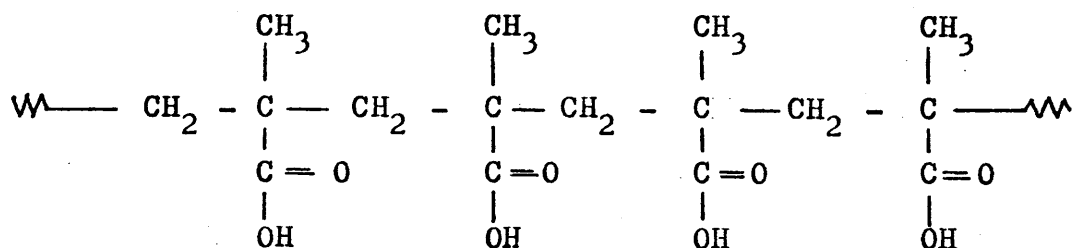
CLASSIFICATION

Polyelectrolytes may be classified electrochemically into one of the following three categories depending upon the nature of its ionization in aqueous solution:-

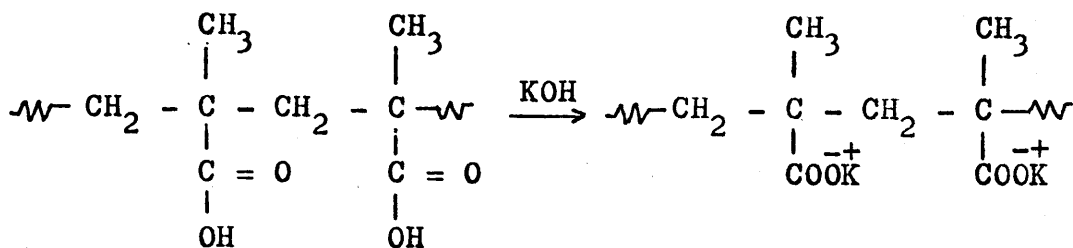
- (a) Polyacid.
- (b) Polybase.
- (c) Polyampholyte.

Polyacids are further classified into weak polyacids and strong polyacids.

Poly(methacrylic acid) is a weak polyacid and a typical synthetic polyelectrolyte, with the repeating structure:-



Ionization of the carboxylic group does not occur in non-aqueous solvents, but aqueous solutions containing the polymethacrylate anion (obtained by adding a base to a solution of poly(methacrylic acid))

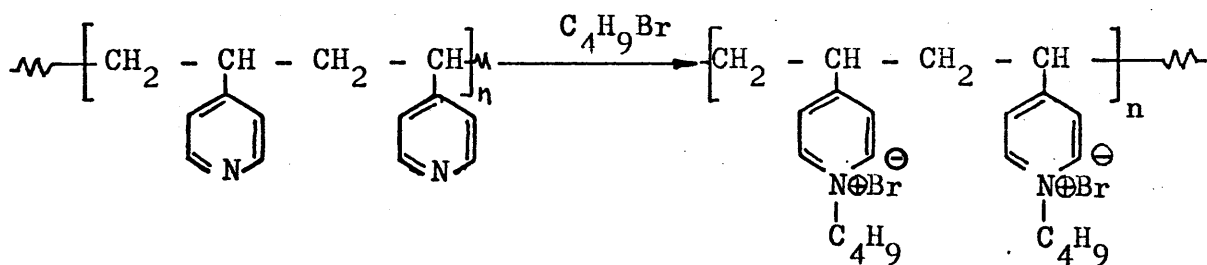


display unique and remarkable properties characteristic of a solution containing charged macroions.

Strong polyacids are highly ionized in aqueous solution throughout the entire range of pH. An example of this type of polyelectrolyte is poly(ethylene sulfonic acid).

Various polybases have been synthesized; examples of weak synthetic polybases are poly(vinyl amine) and poly(vinyl pyridine).

These macromolecules become charged macroions by acquiring protons in acidic solution. When weakly basic poly(4-vinyl pyridine) is quaternized with an alkyl halide, such as butyl bromide, the highly ionized cationic polyelectrolyte poly(4-vinyl n-butyl pyridine bromide) results:-



The properties of such a polyelectrolyte are greatly influenced by the nature of the quaternizing alkyl halide.

Proteins and nucleic acids, by far the most important of the naturally occurring polyelectrolytes, are polyampholytes.

Proteins are polypeptides whose side chains may contain both ionizable acidic and basic groups. The net macromolecular charge on a protein is thus a function of the pH of its aqueous environment. A few synthetic polyampholytes have been prepared, for example, the copolymer of acrylic acid and vinyl pyridine.

Polyelectrolytes may also be classified as either linear or crosslinked. Sulphonation of polystyrene that has been crosslinked with divinyl benzene results in a polyelectrolyte containing negative charges located on a crosslinked matrix of truly macroscopic dimensions. These synthetic crosslinked polyelectrolytes are used as ion-exchange resins.

CATION BINDING IN POLYELECTROLYTES

Alkali metal salts of poly (acrylic acid) and poly (methacrylic acid) are not readily converted to free acid by ordinary dialysis; they require electrodialysis or treatment with ion exchange resins to liberate free acid. Studies of osmotic and transport properties of sodium polyacrylate and other polyacrylates show that the small cations behave as if many of them are bound to the polymeric anion. Workers in the field do not agree on the exact nature of this binding. Some speak of specific binding at a site and interpret their data in terms of the fraction of the cations bound. Others prefer to use the activity co-efficient of the cations to describe the reduced activity.

Apparent ion binding occurs because the strong electrostatic forces surrounding a polymer chain bearing many ionized carboxyl groups cause small positive ions to spend much of their time close to, or bound to, the polymeric anion. Ion binding increases^{1,2} with extent of ionization, with increasing valence of cation and decreasing size of cation, and with increased acid strength of the ionizable groups on the polymer chain. Small ions are more tightly bound than larger ones and divalent ions are more tightly bound than monovalent^{1,2}. In the series of alkali metals, binding in poly (acrylic acid)

decreases in the order.¹ Li Na K Rb.

TACTICITY

During polymerization, successive monomer units become incorporated in a polymer chain with configurations that are the same or opposite to the configurations of the preceding monomer units. In polymers made by free radical polymerization, the distribution of these configurations depends on the monomer, the temperature of polymerization and the solvent. Poly (methacrylic acid) can be converted to poly (methyl methacrylate) by treatment with diazomethane,² and the tacticity of the polyester can be measured by nuclear magnetic resonance spectroscopy. This method for measuring tacticity expresses syndiotacticity as percentage of syndiotactic triads, -ldl- (or -ldl-) and isotacticity as percentage of isotactic triads, -dül- (or -lld-). Lobell and O'Neill,³ showed that poly (methyl methacrylate) made from poly (methacrylic acid) prepared by ordinary free-radical polymerization (dissolved in ethyl methyl ketone and polymerized at 60° in the presence of azobisisobutyronitrile) was 57% syndiotactic. These workers also showed that syndiotacticity can be increased, if the polymerization is carried out at low temperatures.

Bovey⁴ studied tacticity of polymethacrylic acid in detail with the idea that the degree of dissociation of the monomer and polymer may have a significant effect on the stereochemical configuration of the growing chain. He also suggested⁵ that the terminal monomer unit at the growing end of a polymer radical, may become unable to maintain asymmetry, when reaction occurs with a monomer molecule. This terminal monomer unit must decide whether to assume an isotactic or syndiotactic

configuration with respect to the penultimate monomer unit. He found it reasonable to assume that when both the monomer and the polymer growing radicals are negatively charged, as in methacrylic acid polymerization at high pH, coulombic repulsion will tend to favour one mode of addition over the other. Bovey⁴ showed that if methacrylic acid is polymerized in aqueous solution, using potassium persulphate as initiator then syndiotacticity will increase with the rise in pH of the solution. At pH 10, the ratio of isotacticity to syndiotacticity was found to be as low as 0.14.

Schroeder⁶ polymerized sodium methacrylate in water at 60°C, using potassium persulphate as initiator and found that it had an s-value (% syndiotacticity content) of 93 and lithium methacrylate, sodium methacrylate, caesium methacrylate and ammonium methacrylate had s-values of 90, 93, 93 and 92 respectively. He also polymerized these salts in other less polar solvents and found that the s-values were dependent on solvation of monomers. From the above values it seems that the size of the ion also plays an important role in the tacticity, since syndiotacticity is increased as the size of the counter ion increases.

DEGRADATION OF POLYMERS

In the polymer chemistry field the term "degradation" may be used in its most restricted sense to refer to polymer deterioration or in the wider sense to include all types of polymer reactions. In the past forty years the growth of polymer science and technology has been very fast. The deterioration and chemical changes accompanied by the exposure of polymers to heat in both inert and oxidizing

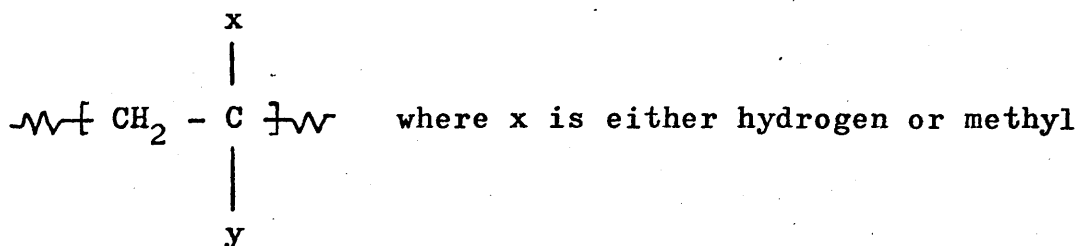
atmospheres has aroused more interest and has been investigated more extensively than that of any other form of energy, such as light, mechanical stress, ultrasonic, ultraviolet or gamma radiation.

Studies on the thermal behaviour of polymers, particularly on their thermal degradation, are of prime importance from a scientific point of view, as they help to reveal the molecular structure, such as the sequence and arrangement of the repeating units, or monomers, and side groups in the polymer or copolymer chain, as well as the nature of the chain ends.

Similarly thermal degradation studies of polymers are of extreme importance from a practical point of view. They not only explain the behaviour of polymers under conditions of high temperatures but also help in selecting the right kind of already existing material for specific uses where high temperatures are encountered, and what is sometimes more important, suggest the design and synthesis of new materials to meet new or existing requirements.

Polymer degradation may be applied to recover monomers from polymers such as methyl methacrylate and this can only be achieved by finding the optimum conditions for efficient reaction. Another useful application of thermal degradation is the preparation of carbon fibres, for example, by heating of polyacrylonitrile at a temperature above 1500°C under vacuum or in an inert atmosphere.

The remainder of this chapter will be devoted to the chemical changes produced by the action of heat on organic polymers of the vinyl type, with the general formula



group and y a functional group.

CLASSIFICATION OF REACTIONS

Thermal degradation has been broadly divided into two categories:-⁷

- (a) Chain scission reactions or depolymerization.
- (b) Non chain scission or substituent reactions.

The first type of degradation process is essentially a depolymerization process and is characterized by breaking of the main polymer chain backbone, so that at any intermediate stage the products are similar to the parent material. The ultimate products are monomer or closely related to it.

In substituent or non chain scission reactions, the substituents attached to the backbone of the polymer chain are eliminated, or modified in such a way that the chemical nature of the repeating units is changed leaving the chain intact.

One or other or both reactions may occur in a polymer chain depending on the polymer, the temperature and the mode of initiation of degradation.

Both types of reactions will be discussed in greater detail individually as these will be encountered in later chapters.

CHAIN SCISSION OR DEPOLYMERIZATION

A large variety of addition polymers depolymerize thermally, and detailed studies have shown quite distinct behaviour. Poly (ethylene) and poly (methyl methacrylate) are the two extremes and will be discussed individually in this section.

Polyethylene:

Montroll and Simha⁸ assumed that since there is a regular, repeated pattern of bond strength throughout the polymer chain, random chain scission is likely to occur. This would produce volatile material, short chain fragments, possessing a similar structure to that of the polymer chain, but of different molecular weight. The upper limit of this material would be the largest molecule which could distil from the hot degradation zone.

The early studies of thermal degradation of poly (ethylene)⁹ showed that the degradation products are a continuous spectrum of hydrocarbon fragments as predicted by the above theory. But in later work,¹⁰ some discrepancies were found. According to the theory, the rate of bond scission should remain constant throughout the degradation, but Oak and Richards¹⁰ found that it decreased with time. They explained this discrepancy by suggesting that there were some weak linkages present in the chain due to traces of copolymerized oxygen.

Oak and Richards found another contrast to Montroll and Simha's theory, as their sample of poly (ethylene) degraded at a much lower temperature than model compounds such as n-hexadecane. This instability was attributed to branching of the polymer chain.

Poly (methyl methacrylate)

Votinov and co-workers¹¹ were the first investigators to study the thermal degradation of poly (methyl methacrylate) under nitrogen at 350, 400 and 450°C. They determined the activation energy 25K cal/mole. The interpretation of their results was in terms of a random scission process of carbon-carbon bonds in chain backbone, but such a process would have given a broad spectrum of molecular fragments, since only monomer is the exclusive product in the 150 - 500°C temperature range, so this initial proposal was not considered applicable to poly (methyl methacrylate).

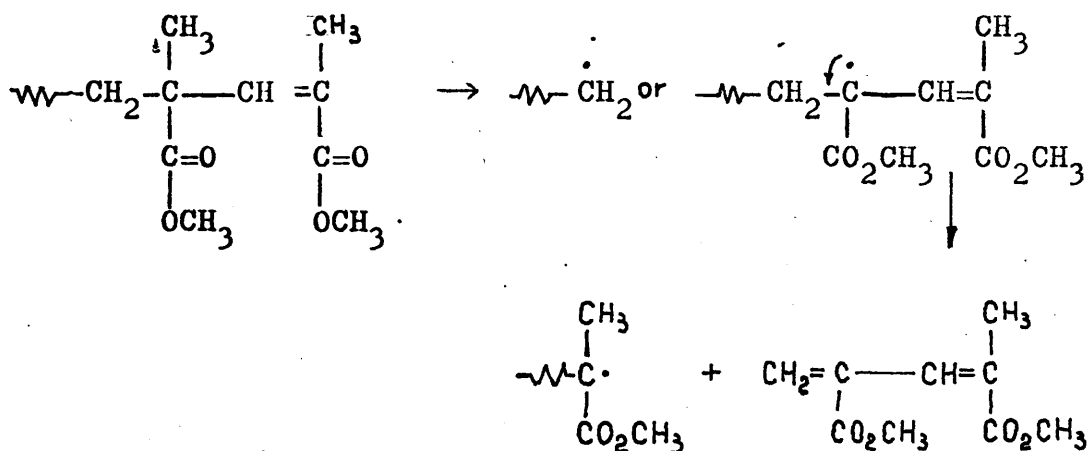
Grassie and Melville,¹² determined the change in molecular weight of the residue formed during the thermal degradation of poly (methyl methacrylate) at temperatures of 160 and 200°C under vacuum. The rate of monomer production was followed and molecular weights of the residues were determined. The quantitative yield of monomer was obtained. The initial stages of such degradations have been proposed to involve the production of a free radical chain end. Grassie and Melville¹³ interpreted the mechanism of thermal degradation of poly (methyl methacrylate) as the formation of free radicals via a random chain scission process, followed by unzipping to monomer. Such an interpretation seems reasonable, since on adding equimolecular amount of 1,4 diamino anthraquinone to the degradation system, the degradation ceased completely, presumably by blocking the radical chain ends, and unzipping to monomer.

Grassie and Vance¹⁴ showed that unstable chain ends are those with a double bond. The termination in the free radical

polymerization has been shown by disproportionation, so that half of the polymer chain has a double bond at one end.

Madorsky¹⁵ and Hart¹⁶ measured the rate of volatilization of poly (methyl methacrylate) of different molecular weights at temperatures in the range of 240-270°C. The activation energy calculated (33K cal/mole) from the rates obtained agreed well with that obtained by Grassie and Melville.^{12,13}

It has not been yet established with certainty that thermal decomposition of poly (methyl methacrylate) involves linkage of head to head type, but the majority of the proposals are based upon the repeat unit derived from the head to tail polymerization of acrylic monomers. Monomer production in the thermal degradation of poly (methyl methacrylate) can be shown by the following scheme:-



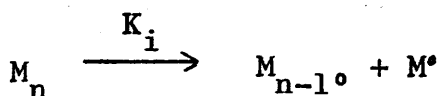
Thereafter the monomer is produced by a similar process.

The thermal degradation of polyethylene, poly (methyl methacrylate) and all intermediate types of behaviour may be described in terms of single free radical reaction, incorporating, initiation, depropagation, transfer and termination.¹⁷

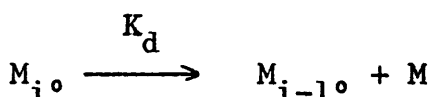
Random initiation:-



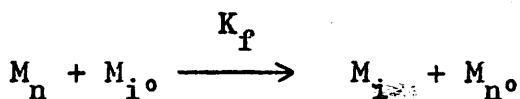
Terminal initiation:-



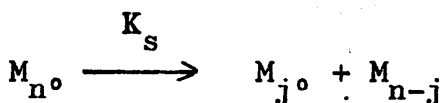
Depropagation:-



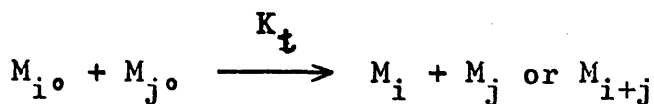
Transfer:-



Scission:-



Termination:-



In these equations n represents the chain length of the starting material and M_i , M_j etc. and M_j^\bullet , M_i^\bullet etc. represent respectively "dead" polymer molecule and long chain radicals, i, j etc. monomer units in length.

EFFECT OF POLYMER STRUCTURE ON DEPOLYMERIZATION

The polymer structure is of fundamental importance in the study of polymer degradation. Wall, Madorsky and their co-workers¹⁶ studied the products and overall rate characteristics of the depolymerization of a variety of polymers and made interesting qualitative correlations between polymer structure and the nature of the depolymerization reaction which occurs.

In general, relative importance of depropagation depends on two facts:- the reactivity of the degrading polymer radical and the availability of a reactive atom (usually hydrogen) in the polymer structure.¹⁷ Therefore transfer is favoured by an active radical and is less likely to take place with a resonance stabilized or sterically hindered radical, while high yields of monomers are produced from polymers which are devoid of tertiary hydrogen atoms.

A comparison of the degradation behaviour of poly (α -deutero styrene, poly (β -deutero styrene), poly (m-methyl styrene), and poly (α -methyl styrene) with that of poly (styrene) shows that the site at which transfer occurs in the production of dimer, trimer and tetramer is as expected, the α -hydrogen atom, which is the most reactive hydrogen atom in the molecule. Therefore substitution of this atom by deuterium resulted in an increase of monomer yield from 42% to 70%.

Transfer is completely suppressed when the hydrogen atom is replaced by a methyl group as in poly (α -methyl styrene) which gives 100% monomer, but the methyl group in the ring has little effect.

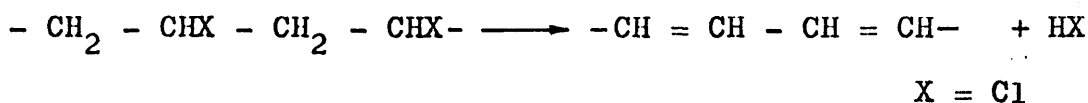
SUBSTITUENT REACTIONS

Among depolymerization reactions there exists the outstanding unifying feature that whatever the detailed mechanism may be the reaction ultimately resolves itself into progressive breaking of the chain backbone. Substituents can modify these reactions, but the essential main chain scission feature remains. These reactions usually occur at relatively lower temperatures, than those at which main chain bonds are broken. Substituent reactions have no comparable unity, since they depend predominantly upon the chemical nature of the appendages to the polymer backbone.

Substituent reactions, which may compete with or supplant chain scission processes, can be classified into three main types:-

- (a) Elimination reactions.
- (b) Ester decomposition.
- (c) Cyclization reactions.

Type (a) is illustrated by poly (vinyl chloride), which eliminates hydrogen chloride, producing a conjugated polyene chain:-

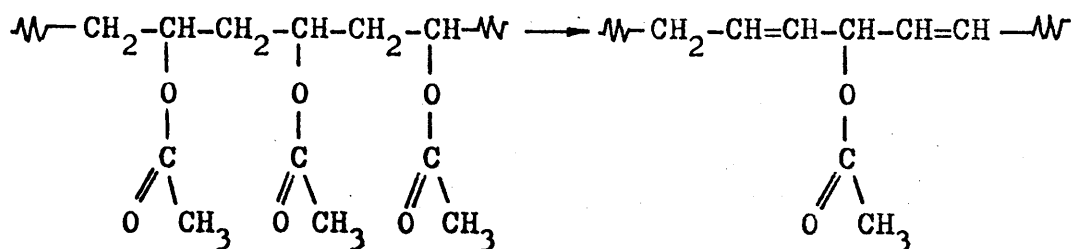


Analogous processes are known where $x = OH, Br, O - \underset{\underset{O}{||}}{C} - CH_3$

The process of elimination of HCl from PVC is not clearly elucidated but theories have been put forward that the process is respectively ionic,¹⁸ molecular,¹⁹ or radical²⁰ in nature.

The role of hydrogen chloride in the degradation of poly (vinyl chloride) has caused a great deal of controversy. Early investigators claimed that it behaved as a catalyst, but this was contradicted by Arlman.²¹ It is now clear that most of the features of degradation of poly (vinyl chloride) may be accounted for qualitatively in terms of the radical mechanism, although there is no general agreement about this interpretation.

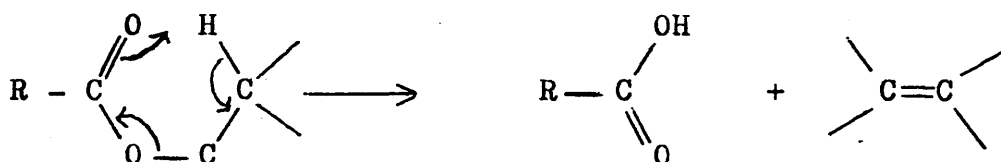
Poly (vinyl acetate) was first studied in detail by Grassie.²² Based upon the rate of acetic acid volatilization, a non-radical chain reaction for the degradation mechanism was proposed. The conjugated structure of the polymeric residue also favours chain reaction rather than random acetic acid removal. Later studies¹⁶ have reported that an almost quantitative yield of acetic acid can be obtained at relatively low temperatures. This evidence would strongly favour the conjugated residue and chain reaction.



Random removal of acetic acid

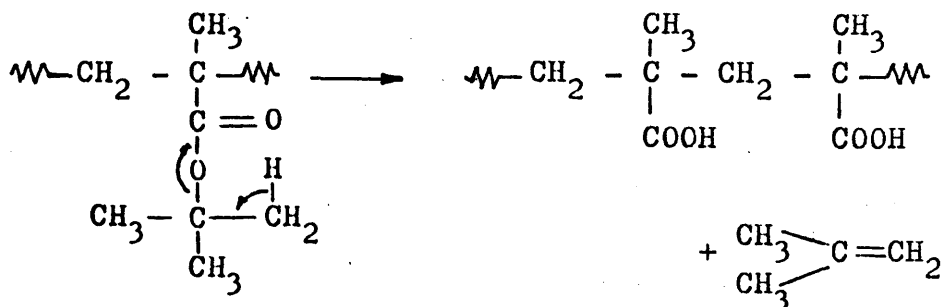
Grassie²² also suggested that once one double bond is formed in the polymer chain, it weakens the bond in the next acetoxy group between the β carbon and hydrogen atoms so that a molecular chain reaction is produced.

In type (b) ester decomposition into acid and olefin is known to proceed by a molecular mechanism, which is facilitated by the six-membered ring interaction existing between the carboxylic group and the β hydrogen of the alcohol residue.



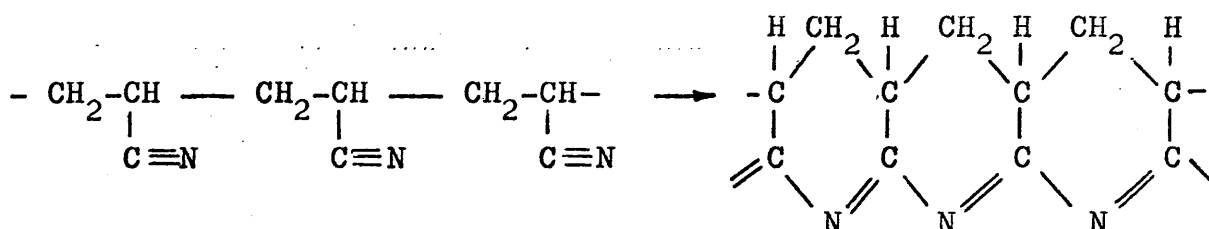
The ease with which the reaction occurs depends on the number of β hydrogen atoms and on the inductive effects of substituents on the alkyl group - that is on the availability of the β hydrogen atom on the alkyl group.^{23,24}

Ester decomposition reactions have been found in short chain esters; poly (t-butyl methacrylate) liberates isobutene leaving poly (methacrylic acid) as the first formed product.²⁵

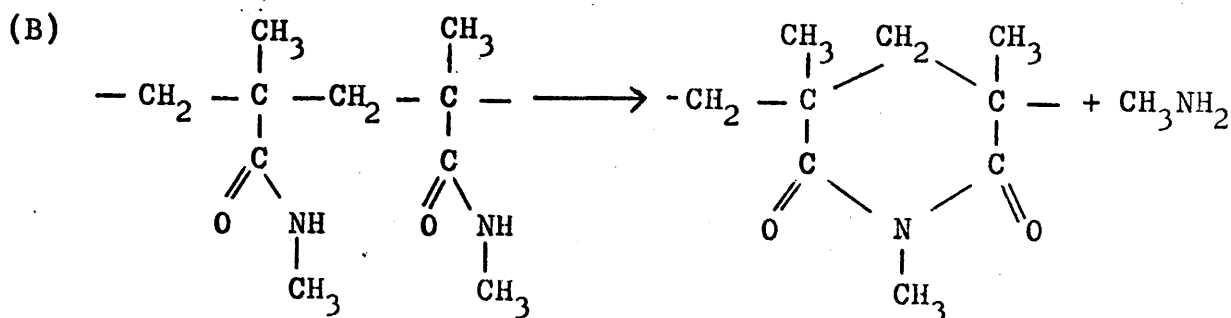
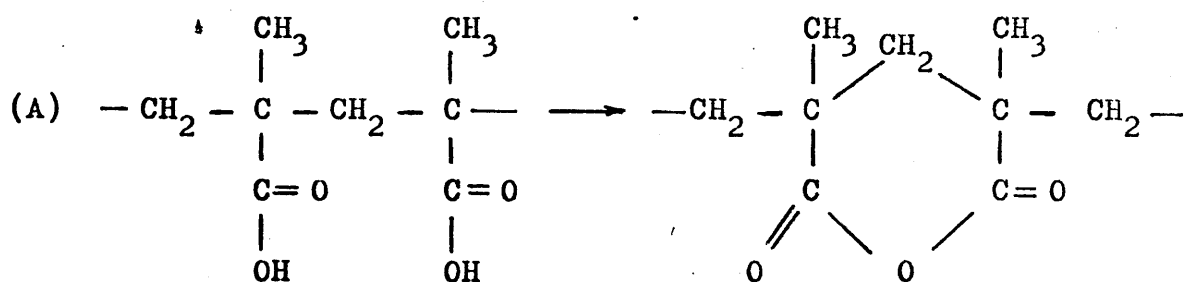


In type (c), the side groups in the polymer chain undergo reaction to give a cyclic polymer structure.

In some polymers, heat induces a rearrangement in the chemical structure without simultaneous evolution of volatile material, as in poly acrylonitrile.^{26,27}



A polymer may also undergo cyclization with concurrent elimination of small molecules, as in poly (methacrylic acid)²⁸ (A) and poly (N-methacrylamide)²⁹ (B).



The mutual interaction of pendant groups may also occur intermolecularly, leading to a crosslinked network. Cyclization reactions are discussed further in a later chapter.

The wide diversity of substituent reactions does not permit a common reaction mechanism to be written. However, several features common to substituent reaction emerge.

- (a) They lead to the formation of products structurally dissimilar to the original polymer.
- (b) The final product (at temperatures above 500°C) is usually a carbonaceous residue, often akin to graphite.³⁰ This is due to the initial formation of cyclic or crosslinked structures, which rather than volatilizing completely may undergo re-orientation, and dehydrogenation to give almost pure carbon.
- (c) Substituent reactions frequently lead to colouration of the residue, due to the formation of conjugated unsaturated structures.
- (d) Substituent reactions often commence at temperatures below those at which depolymerization occurs. The substituent reaction, if allowed to proceed to a sufficient extent, will also inhibit any potential depolymerization process. This is due to the formation of structures which do not permit depropagation processes to pass through them. An example of such behaviour is poly (methacrylonitrile), where cyclization can occur at lower temperatures than monomer production.³¹

GENERAL CONSIDERATIONS

The ultimate aim of studies of thermal degradation is the prediction of the thermal stability of a polymer, given its chemical constitution. Such detailed predictions are not yet feasible, although some generalisations can be made concerning the relationship between structure and thermal stability.

- (a) Polymer molecules often contain labile structural abnormalities, at which points degradation may be initiated, as depolymerization of poly (methyl methacrylate) is initiated by unsaturated chain ends. The presence of small traces of acid in the poly (methacrylonitrile) chain reduces its thermal stability.³² Thus the conditions of polymerization, as well as the history of the monomer used, may have a great influence on the subsequent thermal stability of the polymer.
- (b) Many "model" compound reactions may be converted to chain reactions by the polymer environment. Thus dehydrochlorination of poly (vinyl chloride) is not a reaction which would be expected at the temperature where it is encountered, since secondary chlorides do not decompose at temperatures below 350°C.³³ As a result the study of "model" compounds of low molecular weight cannot be expected to elucidate completely the mechanism of degradation of macromolecular analogues.
- (c) The mechanism of degradation of copolymers cannot necessarily be deduced by extrapolation from the processes occurring in the homopolymers. For instance, copolymers of methyl methacrylate and vinyl chloride are less stable

than either homopolymer liberating methyl chloride as a product at temperatures as low as 150°C.³⁴

- (d) Ionic or "Ionpair" intermediates may be possible in solution degradation or in highly polar polymers, such as polyelectrolytes. But the formation of discrete ions in decomposing organic polymers is unlikely, since the charge cannot be delocalised by solvation, and the dielectric constant of molten polymer is generally too low to support charge separation. Most polymer degradation mechanisms are therefore believed to occur via "radical" or molecular pathways involving uncharged intermediates.

Previous work on salts of poly (methacrylic acid)

Since all naturally occurring polyelectrolytes are found in an aqueous environment, most of the chemical research in this field has been directed towards an understanding of polyelectrolyte behaviour in aqueous solutions. Various salts of methacrylic acid have been polymerized in aqueous solution,^{35,36} but these were not characterized by any of the spectroscopic techniques or by chemical analysis. Shu-Furukawa and co-workers³⁷ were the first who degraded calcium and barium salts of poly (methacrylic acid) and reported only one cyclic ketone. But in their later studies,^{38,39,40} they reported twelve ketones and suggested the mechanism of degradation of salts of poly (methacrylic acid). This will be discussed further in a subsequent chapter.

One related polymer, the behaviour of which is known, is poly (methacrylic acid). The thermal degradation has been studied by Grassie and Grant,²⁸ who found that on heating, only a trace amount of monomer was produced, the main course of degradation being anhydride formation, and on further heating, rapid decomposition to carbon dioxide and volatile hydrocarbons.

Aim of this work

The very rapid and steady progress in the field of synthetic polyelectrolytes' applications in industry naturally stimulated further interest in the problems of synthesis and thermal stability of producing this type of polymer.

The intention was to prepare a series of metal methacrylates and after polymerization, to compare the processes of degradation of the resulting polymers and elucidate degradation mechanisms.

CHAPTER TWO

APPARATUS AND EXPERIMENTAL TECHNIQUES:

The description of the apparatus and techniques employed in the present studies is given in this chapter. Details of monomer and polymer preparation, history, characterization of materials will be described in appropriate chapters.

THERMAL VOLATILIZATION ANALYSIS (TVA)

Thermal degradation of many polymers has been studied using TVA, which has been the subject of a number of publications^{17,41-45} and is now a well established technique of thermal analysis. As TVA was widely used in this work, it is desirable to give a full description of apparatus and its operation.

PRINCIPLE OF TVA

TVA involves a continuous measurement of the pressure exerted by the volatile products as they are released from the heated polymer. Degradation is carried out under high vacuum conditions and the volatile products are thus continuously pumped from the heated sample. The volatiles

pass to a cold trap and the response of a Pirani gauge placed between sample and trap is recorded continuously as a function of oven temperature.

The Pirani response is a measure of the rate of volatilization of the sample.

In Fig.2.1 page 24 a schematic picture of the basic TVA layout is given, while in Fig.2.2, page 24 details of the sample heating assembly are shown. The polymer, usually in the form of a fine powder or as a film cast from a suitable solvent, is heated on the base of a glass tube, 20 cm long and 4.5 cm diameter, constructed from a pyrex SRB40 socket. The top of the tube and the greased socket joint are cooled by a water jacket (cold ring) during the experiment. Heating is carried out by using a Perkin Elmer F11 oven equipped with a linear temperature programmer, by which a sample can be heated isothermally or linearly from ambient temperature up to 500°C at heating rates from 1 to 40°C/min. The oven temperature is recorded using a chromel-alumel thermo-couple, fixed near the base of the tube. Sample temperatures are determined by a calibration procedure which involves continuous measurement of the temperature differential across the base of the tube as the temperature is raised, as discussed subsequently.

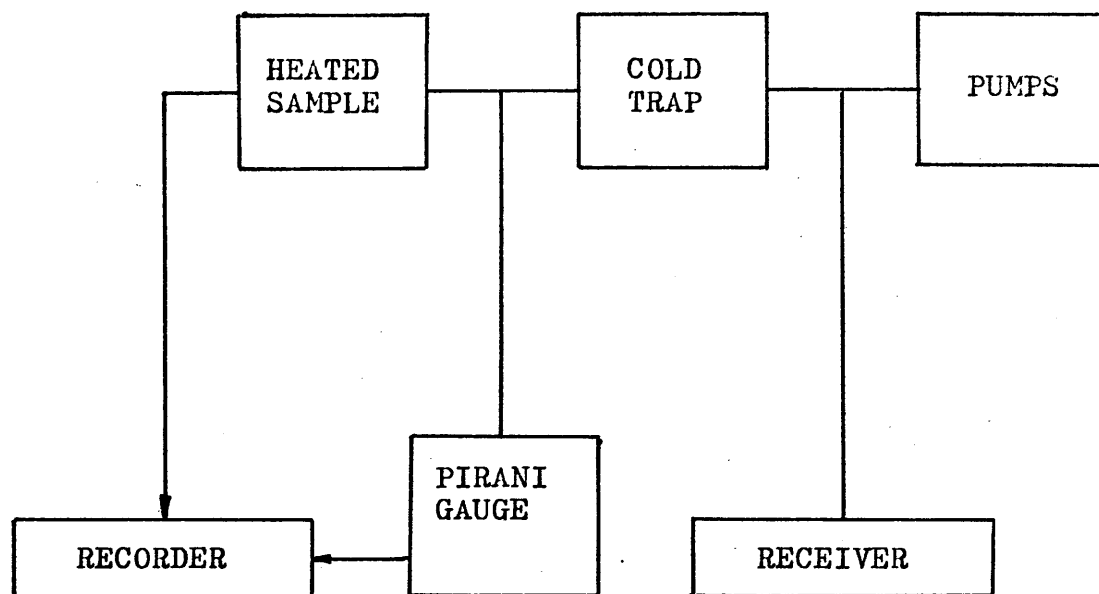


Fig. 2.1 Schematic layout of basic TVA apparatus

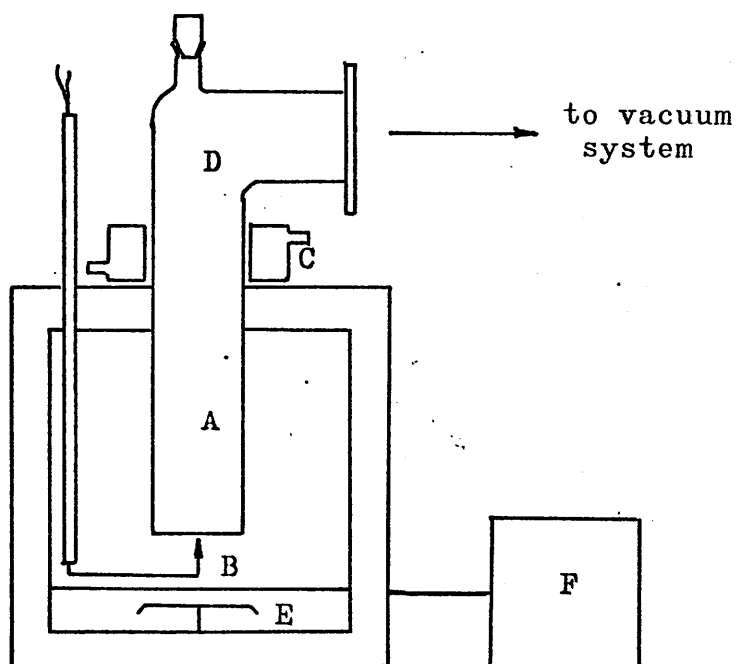


Fig. 2.2 Oven arrangement for TVA

- A Degradation tube
- B Chromel-alumel thermocouple
- C Cooling jacket
- D Removable socket joint
- E Oven fan
- F Temperature programmer

DIFFERENTIAL CONDENSATION TVA

This is a modification^{44,45} of the basic TVA system to allow differential condensation of volatile products. The principle involved is the same, pirani gauge heads used to register the transfer of volatile degradation products from the heated sample to a liquid nitrogen trap (-196°C).

A schematic diagram is shown in Fig. 2.3, page 26. The product stream may pass through four equivalent routes, each with a secondary cold trap, operating usually at four different temperatures, 0 , -45° , -75° , -100°C respectively. After each of these traps is placed a pirani gauge, which measures the pressure exerted by the volatile products which are not condensed by that particular trap and a liquid nitrogen trap. A fifth pirani gauge is positioned after one of the liquid nitrogen traps. The outputs from the five pirani gauges are fed into a multipoint recorder via a multi-gauge head unit, where they are recorded in conjunction with the output from the oven thermocouple. Thus volatiles from the heated sample may be fractionated according to their condensability at each of the five temperatures and a differential condensation TVA thermogram obtained.

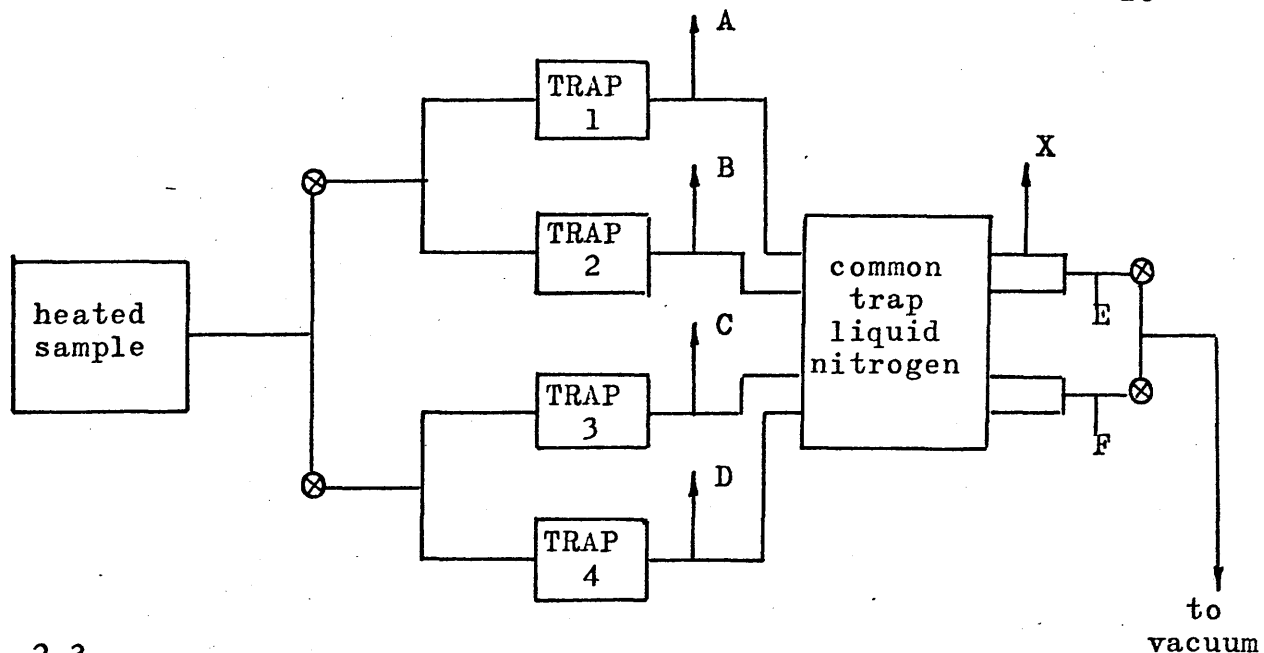


Fig. 2.3

Normal working temperatures ($^{\circ}\text{C}$): 0, -45, -78, -100

A, B, C, D are Pirani gauge heads

E, F are sample receiving tubes as IR gas cell

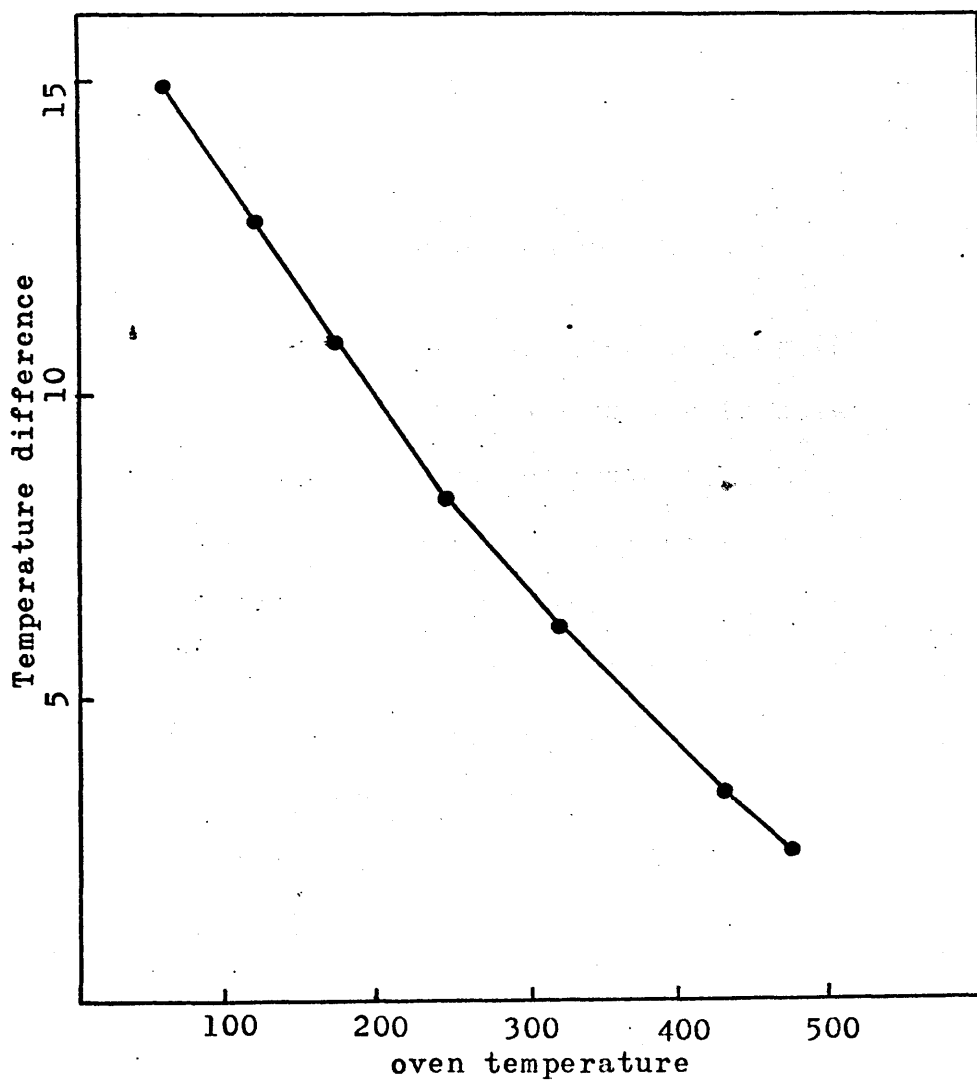


Fig. 2.4 Temperature calibration graph

PRODUCT COLLECTIONS

The products arising from degradation of a sample in the TVA apparatus can be divided into two main categories:-

- (a) The involatile residue.
- (b) The volatile products, which can be further classified into three classes:-
 - (i) Those products volatile at the temperature of degradation but involatile at room temperature (the cold ring fraction).
 - (ii) Substances volatile at the temperature of degradation but involatile at the cold traps temperatures (0° , -45° , -75° , -100°C), (condensable).
 - (iii) Products volatile even at liquid nitrogen temperature (196°C) (non-condensable).

Category (a), the residue, remaining on the tube base, was subjected to infra red spectroscopy to determine the nature of the functional groups present.

Products of type (b)(i) which were found to collect on the upper portion of the degradation tube at the area cooled by the water jacket (Fig. 2.2) could be collected for subsequent analysis by wiping this region of the tube with a tissue moistened with a suitable solvent. Solvent extraction could then give a solution of sufficient concentration to permit an I.R. spectrum to be run. In the present studies some of the cold ring fraction products were also removed as solids for I.R. examination in KBr discs by scratching the cold ring with a spatula.

The products of type (b)(ii) can be isolated in the cold traps by closing the taps and then distilling into a receiver, and can be identified by I.R. spectroscopy or by gas chromatographic techniques.

The non-condensables cannot be isolated in liquid nitrogen as they are pumped through the cold trap system under the continuous pumping conditions of TVA. The non-condensables (e.g. methane, carbon monoxide, hydrogen) can be identified using an alternative closed system, which consists of an I.R. gas cell and cold trap to condense the less volatile substances. Such a typical system has been described by McNeill and Neil.⁴⁶

TEMPERATURE CALIBRATION

The temperature recorded during an experiment is that of the fixed thermocouple B shown in Fig. 2.2 and this is always higher than the actual temperature of the interior of the base of the degradation tube. This thermal lag, which is a function of temperature, heating rate, particular degradation tube, and position of the oven thermocouple, is caused by the insulating effect of pyrex glass, and loss of heat from the tube to the cooling jacket.

The internal base temperature may be obtained by calibration with a second, internal, thermocouple, with its function in contact with the tube base. A small bead of Apiezon "L" grease is used to improve thermal contact between metal and glass and to simulate molten polymer.⁴² The temperature differential between oven and tube thermocouple is

plotted as a function of oven temperature (Fig. 2.4). It is obvious from the graph that thermal lag does not increase with increasing temperature, but falls to a plateau in the higher temperature region. This temperature lag was found to be reproducible for the particular tube, and for the particular heating rate (i.e. $10^{\circ}\text{C}/\text{min}$). The large mass of the tube, as compared with that of polymer sample, means that the thermal capacity of the tube will be sufficiently great to ensure that thermal effects which may be present during polymer degradation, have little influence on the sample temperature.

LIMITATIONS OF TVA

Only those products which are sufficiently volatile to reach the Pirani filament are recorded in a TVA thermogram. This means that not all the processes detected by thermogravimetry can be detected by TVA. In this respect TVA is similar to other gas evolution analysis methods, such as MTA or pyrolysis/glc. However, a TVA thermogram is obtained because of the great sensitivity of the Pirani gauge, even if only a small proportion of the weight of the material is lost.

As with TGA kinetic parameters can be obtained, but in this study poly (methacrylate salts) were found to present a complicated degradation pattern, so TVA has in this instance been used only for qualitative purposes.

ADVANTAGES OF TVA

In TVA the temperature gradients within the sample are minimised as the sample is heated either in the form of a very thinly distributed powder or a film, and the temperature of the sample can be accurately measured because of the massive degradation tube. Furthermore, the large area available for the sample and the continuous and efficient removal of the volatiles from the sample, are factors which tend to reduce the chance of diffusion controlled processes and secondary reactions of products occurring in TVA.

THERMOGRAVIMETRIC ANALYSIS (TGA)

As the Du Pont 950 thermogravimetric analyzer cannot be used under high vacuum conditions, all the TGA experiments were carried out in an atmosphere of nitrogen.

The boat shaped platinum sample holder measured 1 x 0.5 x 0.25 cm deep, and the temperature measuring thermocouple was placed 0.1 cm from the sample holder. The rate of gas flow was 70 c.c./min, and the sample size was about 10 mgs. Programmed work was carried out using a heating rate of 10°C/min, the sample being heated from ambient to 500°C. Isothermal conditions and different atmospheres were also employed in some experiments. The observations obtained from TGA are in agreement in most cases with data obtained from TVA, although because of the different conditions used, these techniques are not strictly comparable.

Some of the differences observed in TGA and TVA data will be discussed in appropriate chapters.

DIFFERENTIAL THERMAL ANALYSIS (DTA)

A Du Pont 900 instrument was used to obtain DTA curves. Powdered polymer (10 mgs) was packed into a small glass tube 25 mm long by 4 mm diameter and a chromel-alumel thermocouple was forced down so that the junction pierced the polymer mass. The reference junction was in an identical tube, containing a quantity of small glass beads, similar in weight to the sample. Sample and reference tubes fitted into a heater block contained in a glass dome through which nitrogen passed at a flow rate of 70 c.c./min. Heating was at 10°C/min up to a temperature of 500°C.

MASS SPECTROSCOPY ANALYSIS

This was carried out on non condensable degradation products using an AEI MS12 mass spectrometer operated at 20 ev. Products collected under vacuum were directly expanded into the spectrometer.

INFRARED SPECTROSCOPY

Qualitative and quantitative spectra were recorded on a Perkin Elmer 257 spectrophotometer. Polymer samples and residues were examined as KBr discs, cold ring fractions were run either in solution (chloroform or carbon tetrachloride) or as KBr discs and volatile products were examined in the gaseous phase.

A Perkin Elmer 225 spectrophotometer was used to run the spectra for investigations of residues to observe the presence of metal oxide.

QUANTITATIVE INFRA RED OF GASES

The gases were analysed quantitatively by infra red spectroscopy using the apparatus in Fig. 2.5. It consists of a simple manometer and a gas cell. The whole system is evacuated to a pressure of less than 10^{-5} Torr, then taps A and C are closed and tap D of the reservoir R containing the known gas is opened. Once a considerable amount of gas has entered the gas cell and manometer, the tap D is closed and the manometer is read in mm of Hg, which gives the pressure of the gas in the cell. The gas cell is then separated from the line and the spectrum of gas is obtained. In this way the spectra of standard gases were run at different pressures and the peak heights were measured and graphs obtained of optical density of the peak against pressure of the gas on the manometer. The calibration plots are given in Fig. 2.7, 2.8 and 2.9.

The infra red detectors were flushed with oxygen free nitrogen at the rate of 100 c.c./min, half an hour before the spectra were run and flushing was continued during the run. These precautions enable quantitative analysis of carbon dioxide in the atmosphere.

The total amount of gas recovered from the degradation products can be found as follows.

$$PV = nRT$$

where P = Pressure

V = Volume of the gas cell

R = Gas constant

T = The absolute temperature

n = No. of moles of gas present.

The volume of the gas cell can be found by measuring the inner diameter "D" of the cell (4.1 cm) and the length of the cell "L" (10 cm) as:-

$$\begin{aligned}\text{Volume of the cell} &= \frac{\pi D^2 L}{4} \\ &= \frac{\pi (4.1)^2 \times 10}{4} = 130.27 \text{ ml}\end{aligned}$$

Similarly the volume of the limb "G" shown in Fig. 2.5 can be found, which is 2.35 ml. Thus total volume of the cell = $130.27 + 2.35 = 132.62 \text{ ml} = 1.3262 \times 10^2 \text{ ml}$.

In all experiments room temperature was taken as 298°K and the gas constant $R = 6.24 \times 10^3 \text{ ml} \times \text{cm.Hg/mole} \times ^\circ\text{C}$.

Therefore for the system:-

$$n = \frac{1.3262 \times 10^2}{6.24 \times 10^3 \times 298} \times P$$

$$\text{or } n = 7.1 \times 10^{-6} P$$

P is in units of cm.Hg.

The standard samples of carbon dioxide, isobutene (British Oxygen Ltd) and ammonia (I.C.I.) were used for calibration. Ammonia was distilled into a reservoir under vacuum over metallic sodium to free it of moisture.

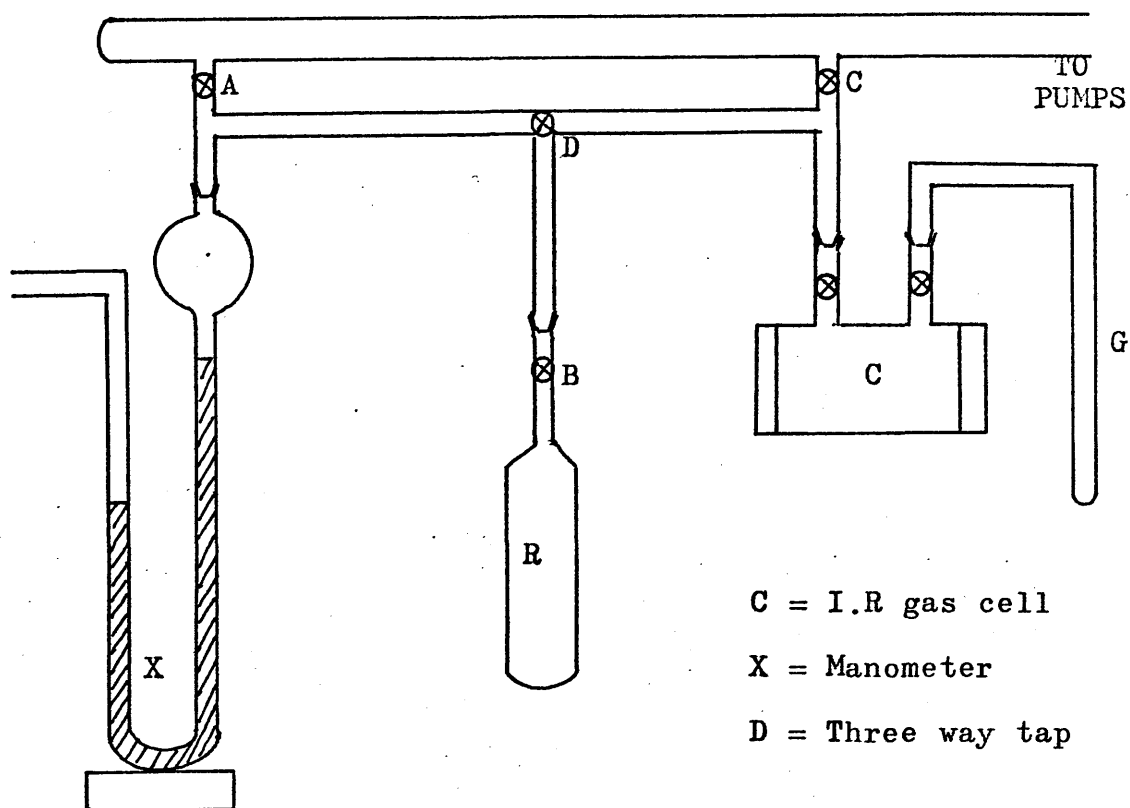


Fig. 2.5 Arrangement for quantitative analysis

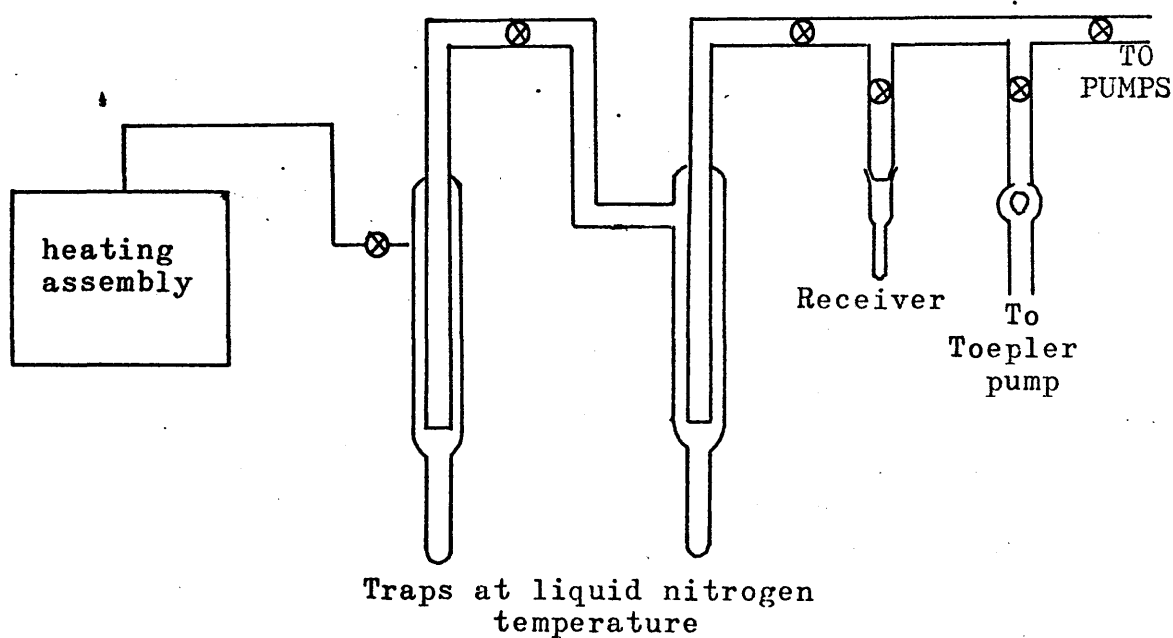


Fig. 2.6 Arrangement for collection of products for quantitative analysis

Hydrogen cyanide, cyanic acid and dimethyl ketene were synthesized in the laboratory as described below.

HYDROGEN CYANIDE⁴⁷

50 gms of concentrated sulphuric acid, 20 ml of H_2O , 1 gm of $FeSO_4$ and a few boiling stones, were heated in a long necked round bottom flask on a water bath to $90^\circ C$ and a solution of 50 gms of NaCN (BDH) in 60 ml of H_2O was carefully added dropwise. After one hour the water bath was heated to boiling and HCN was driven off through the condenser, containing calcium chloride, into the receiving flask which was cooled with ice salt mixture. The receiver was then removed, and HCN was fractionally distilled under high vacuum to obtain a sample free from CO_2 and moisture.

CYANIC ACID⁴⁷

Cyanic acid was obtained by degrading cyanuric acid (trimer of cyanic acid) in the TVA apparatus. 300 mgs. of dehydrated cyanuric acid (BDH) (dried under vacuum at $60^\circ C$ for 16 hours) were placed at the base of the TVA tube, and the system was evacuated to 10^{-5} Torr. The trimer was heated at the rate of $5^\circ C/min$ up to $300^\circ C$, then $40^\circ C/min$ up to $500^\circ C$ under continuous evacuation. Some of the trimer sublimes, but most of it decomposes to $HNCO$. The sublimed part is collected at the cold ring of TVA, and the gaseous fraction is condensed into a liquid nitrogen trap. The resulting product was fractionally distilled on the vacuum line and the infra red spectrum showed the absence of HCN and CO_2 (Fig. 2.10).

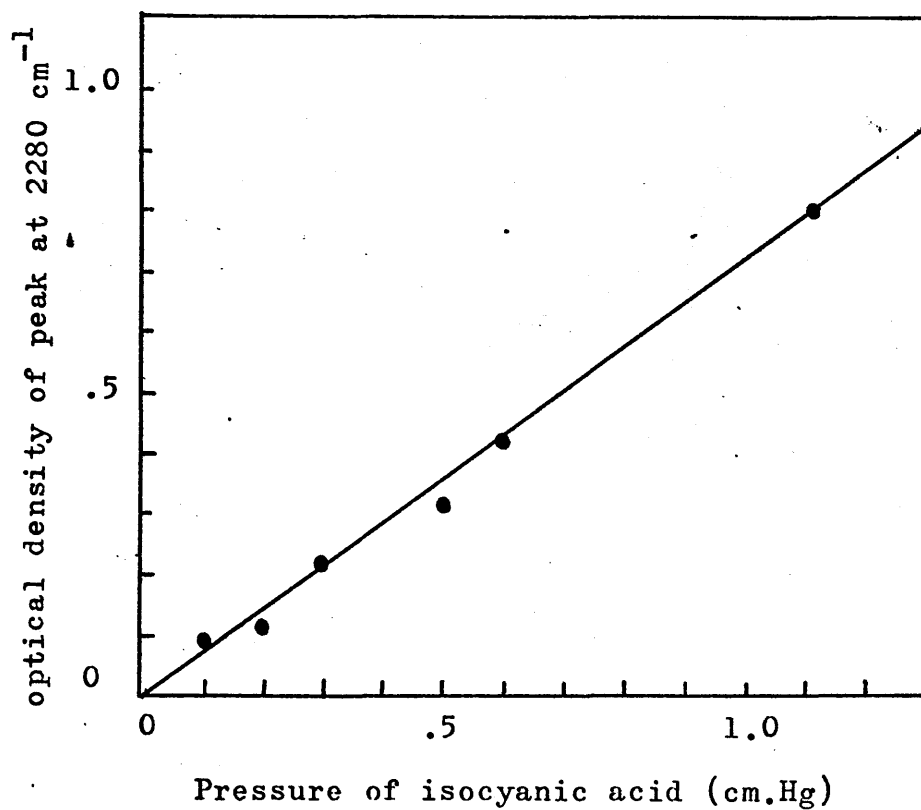
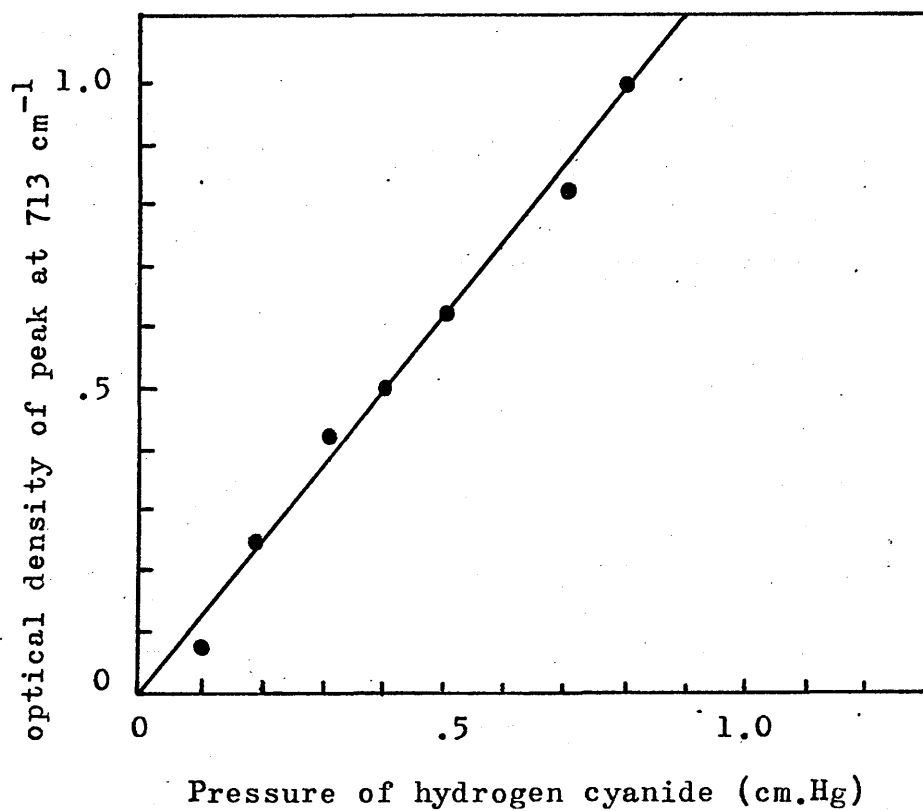


Fig. 2.7 Infra-red calibration curves for hydrogen cyanide and isocyanic acid.

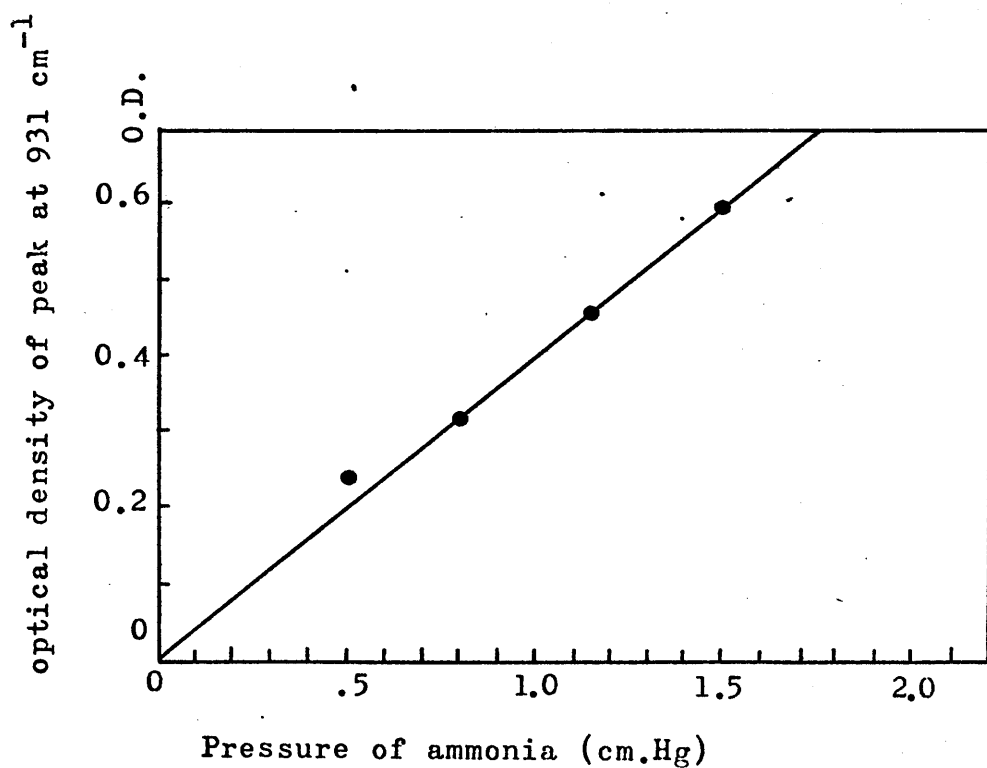
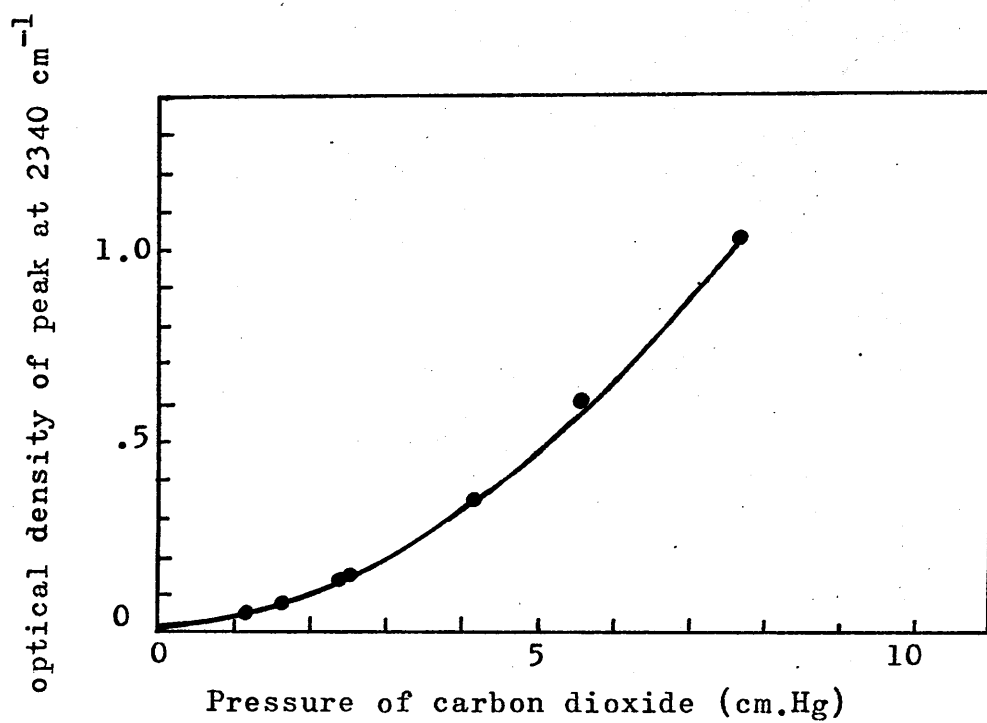


Fig. 2.8 Infra-red calibration curves for carbon dioxide and ammonia.

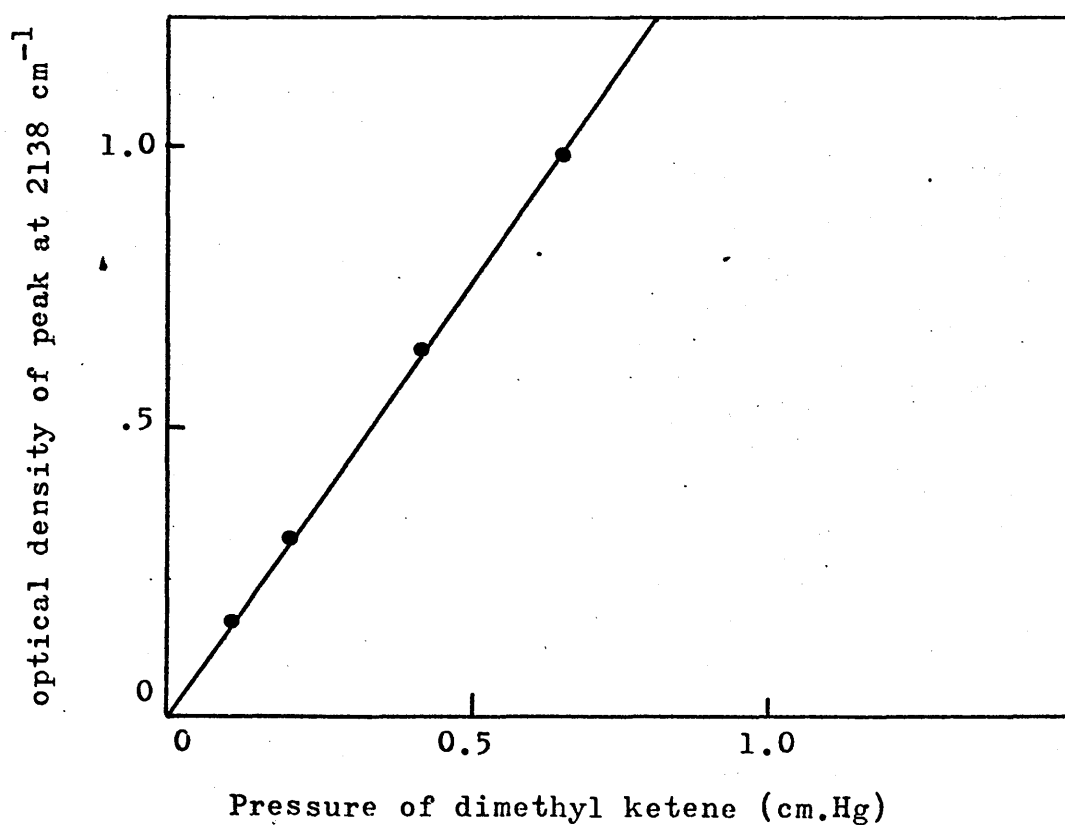
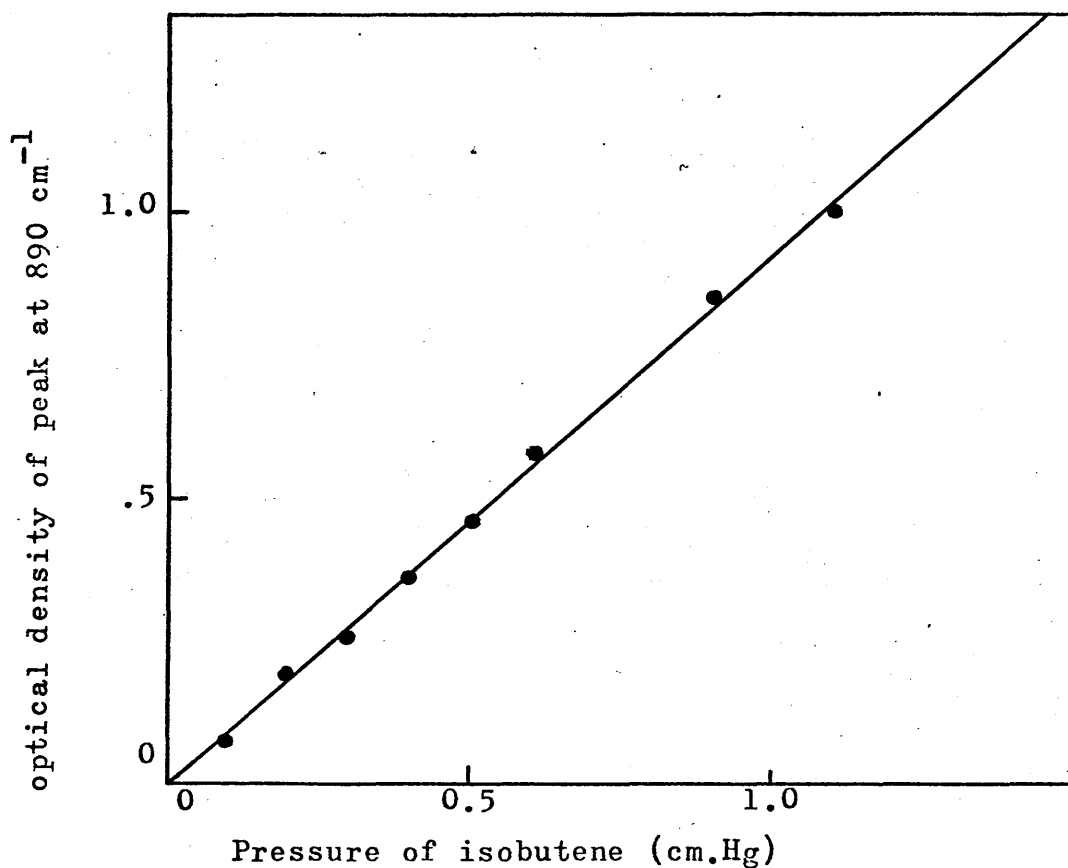


Fig. 2.9 Infra-red calibration cruves for isobutene and dimethyl ketene.

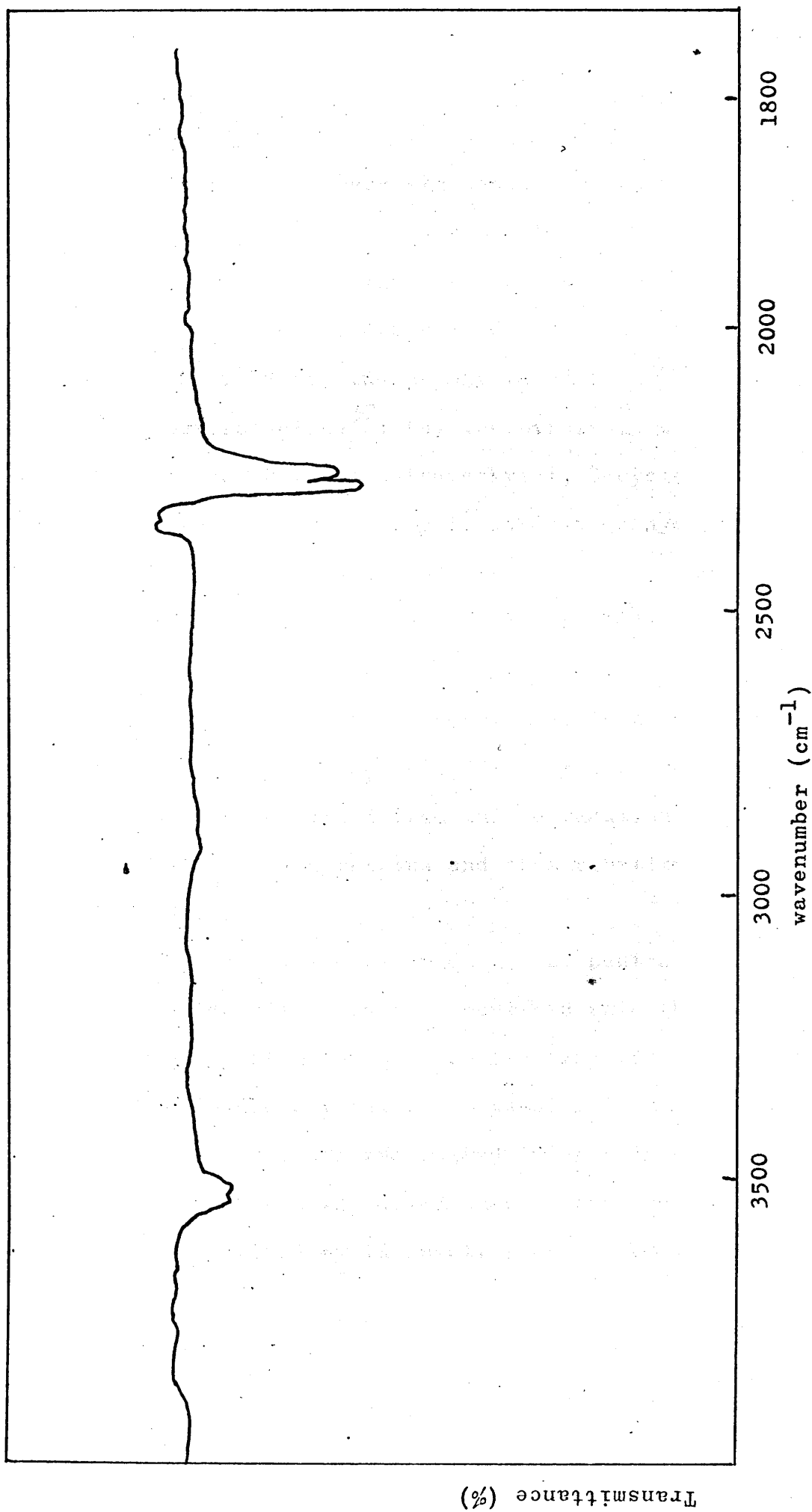


Fig. 2.10 IR spectrum of isocyanic acid

Transmittance (%)

DIMETHYL KETENE

Dimethyl ketene has been synthesized by various methods. These methods were; (a) the treatment of α -bromo isobutyryl bromide with zinc^{48,49}; (b) the pyrolysis of isobutyryl-phthalimide⁵⁰; (c) the pyrolysis of dimethyl malonic anhydride at 180°C⁵¹; (d) the pyrolysis of α -carbomethoxy- α , β -dimethyl- β -butyrolactone⁵²; (e) the pyrolysis of the dimer of dimethyl ketene (2,2,4,4-tetramethyl 1, 3 cyclobutanedione)⁵³; (f) and the pyrolysis of isobutyric acid and anhydride at about 700°C.⁵⁴

Preparations of dimethyl ketene by methods other than the pyrolysis of isobutyric anhydride generally yields greater amounts of impurities and these methods also involve the lengthy synthesis of the parent compounds. In the present studies dimethyl ketene was obtained from the degradation of magnesium isobutyrate in the TVA apparatus and thus constitutes a synthesis of dimethyl ketene.

Magnesium isobutyrate was prepared by neutralizing 4.0312 gm of magnesium oxide with 17.6 gm isobutyric acid (Hopkin and Williams) in 50 ml of methanol. On standing for sixteen hours this solution yielded crystals of magnesium isobutyrate. The salt was then filtered off and washed twice with analar acetone. The recrystallized salt was dried under vacuum at 60°C for 24 hours and characterized by IR spectroscopy. 200 mg of magnesium isobutyrate were degraded up to 500°C at a rate of 10°C/min in the TVA apparatus. During degradation some of the salt sublimes and accumulates as cold ring products in the TVA

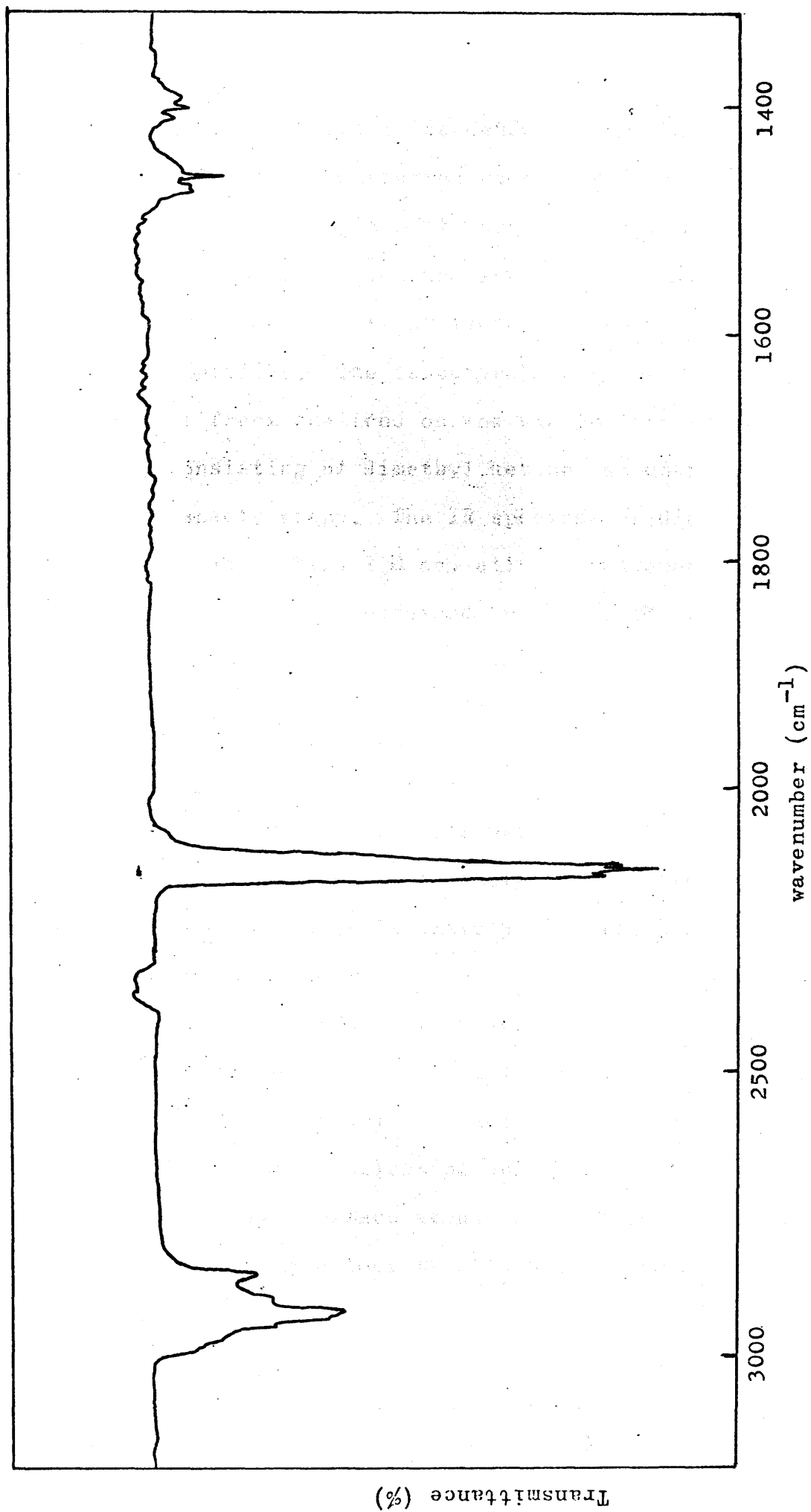


Fig. 2.11 IR spectrum of dimethyl ketene

tube. The gaseous product is condensed in the liquid nitrogen trap and subsequently transferred under vacuum to a receiver. Gas chromatography, using a 6 ft long column (containing 13 $\frac{1}{2}$ % B.M.E.A. and 6 $\frac{1}{2}$ % bi-2-ethyl-hexyl sebacate on chromosorb), indicated that trace amounts of isobutyraldehyde only were present as impurities. The isobutyraldehyde was removed by two successive fractionations on the vacuum line and the distillate, consisting of dimethyl ketene was characterized by infra red spectroscopy. The IR spectrum of dimethyl ketene obtained is given in Fig. 2.11 and all the fundamentals shown are consistent with those obtained by Fletcher and co-workers,⁵⁵ who reported extensively on the IR spectrum of dimethyl ketene.

GAS CHROMATOGRAPHY

For the most part g.l.c. data were collected using a Perkin Elmer F11 instrument with thermal conductivity detector. The gases were analysed qualitatively by using a Microtek G.2000 research chromatograph.

The degradation products from the metal salt polymers were found to contain a mixture of about twenty different liquid products. The boiling points of these ranged from 50°C to 160°C, so causing some problems of collection. As the TVA apparatus has a large surface area, so the higher boiling volatile products take a long time to be condensed in the receiver. To overcome this problem, a new arrangement was designed for the collection of volatile products having the minimum possible surface area. The arrangement is shown in

Fig. 2.6. The heating assembly is the same as described in the case of the TVA system in Fig. 2.2. Due to a large variety of volatile products, various columns were employed as given in Table 2.1.

Quantitative data for the liquid products was obtained by adding a known weight of a suitable material as an internal standard to a weighed quantity of liquid products. Several mixtures of pure samples of each of the products were made up with known amounts of the internal standard and run on the chromatograph to determine the sensitivities of the product compounds relative to the standard. The sensitivity factor (K) may be defined such that,

$$K = \frac{A_s W_a}{W_s A_a}$$

where W_a , W_s are weights of compounds and solvents,

A_a , A_s are the areas of the peaks on the chromatograph.

Measurements of peak areas were carried out by peak cut method.

Once the sensitivity factor is found the weight of a sample is found from a chromatogram using the relation.

$$W_a = K \frac{W_s A_a}{A_s}$$

In all cases N-butyl alcohol was used as internal standard.

Three typical graphs for determining the sensitivity factors are given in Fig. 2.12, and 2.13. These graphs are of an aldehyde, a low boiling ketone, and a high boiling ketone.

The sensitivity factors for various compounds will be tabulated in Appendix "A".

TABLE 2.1G.L.C. Columns Used for Investigation ofDegradation Products

| Columns | Programme | Use | Detector |
|---|--|----------------------|----------------------|
| 13% $\frac{1}{2}$ B.M.E.A. + 6% $\frac{1}{2}$ bi-2-ethyl-hexyl sebacate on chromosorb. P, 80-100 mesh 6 ft. long, $\frac{1}{8}$ " diameter. | Isothermal at 50°C | Aldehydes | Thermal Conductivity |
| " | Isothermal at 60°C | Low boiling Ketones | " |
| " | Isothermal at 70°C | High boiling Ketones | " |
| 15% silicone grease on chromosorb. P, 80-100 mesh, 6 ft. long, $\frac{1}{8}$ " diameter. | | Ketones | " |
| 10% PEG 400 on chromosorb. P, $\frac{1}{4}$ " diameter, 6 ft long | 50° C Isothermal for $\frac{1}{2}$ hour, then programmed 10°C/min to 90°C. | Ketones | Flame ionization |
| Silica gel. 6 ft. long. $\frac{1}{4}$ " diameter | 50°C Isothermal for 15 min. then programmed 10°C/min up to 150°C. | Gases | " |

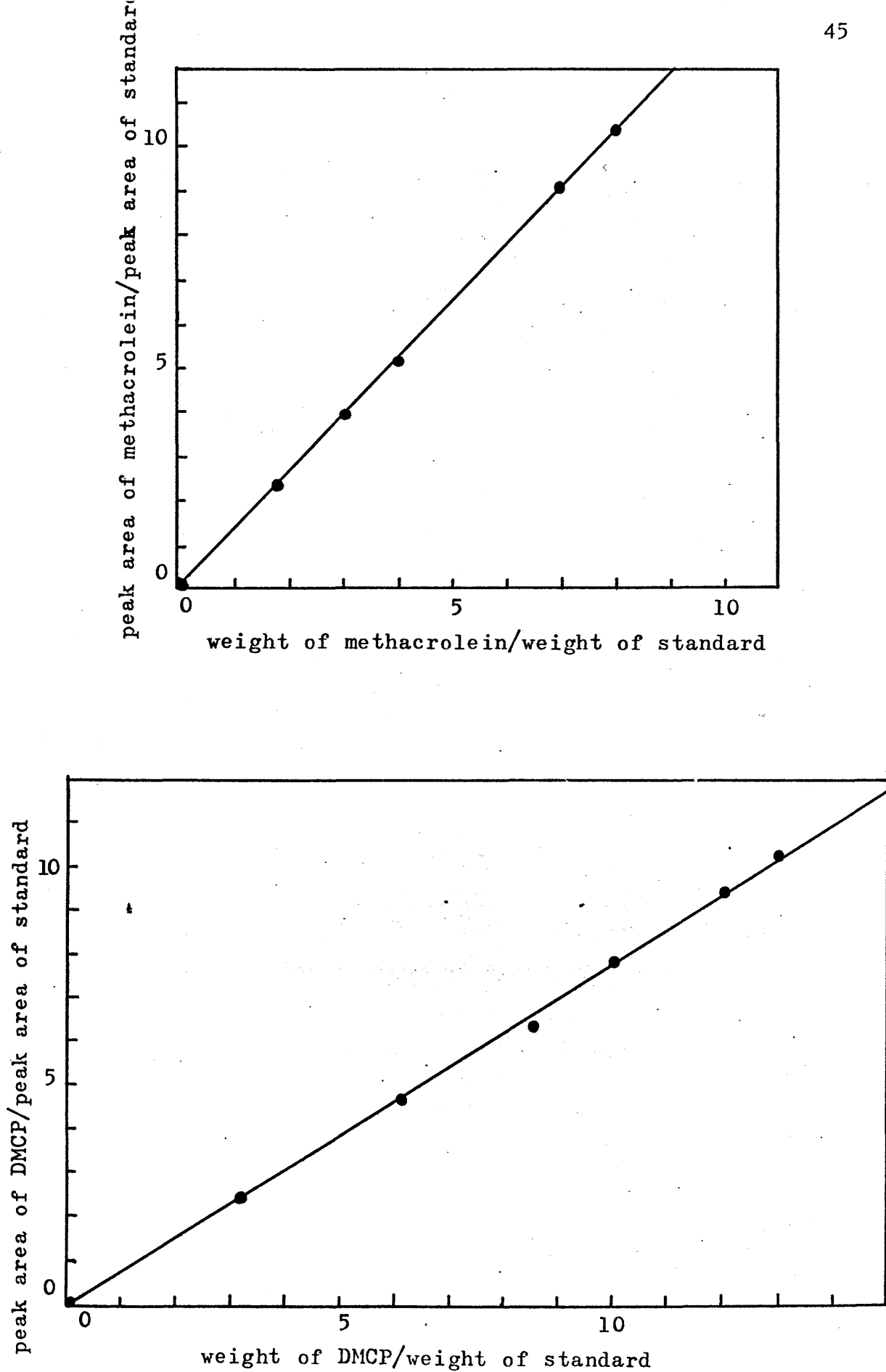


Fig. 2.12 Glc calibration curves for methacrolein and dimethyl cyclopentanone (DMCP)

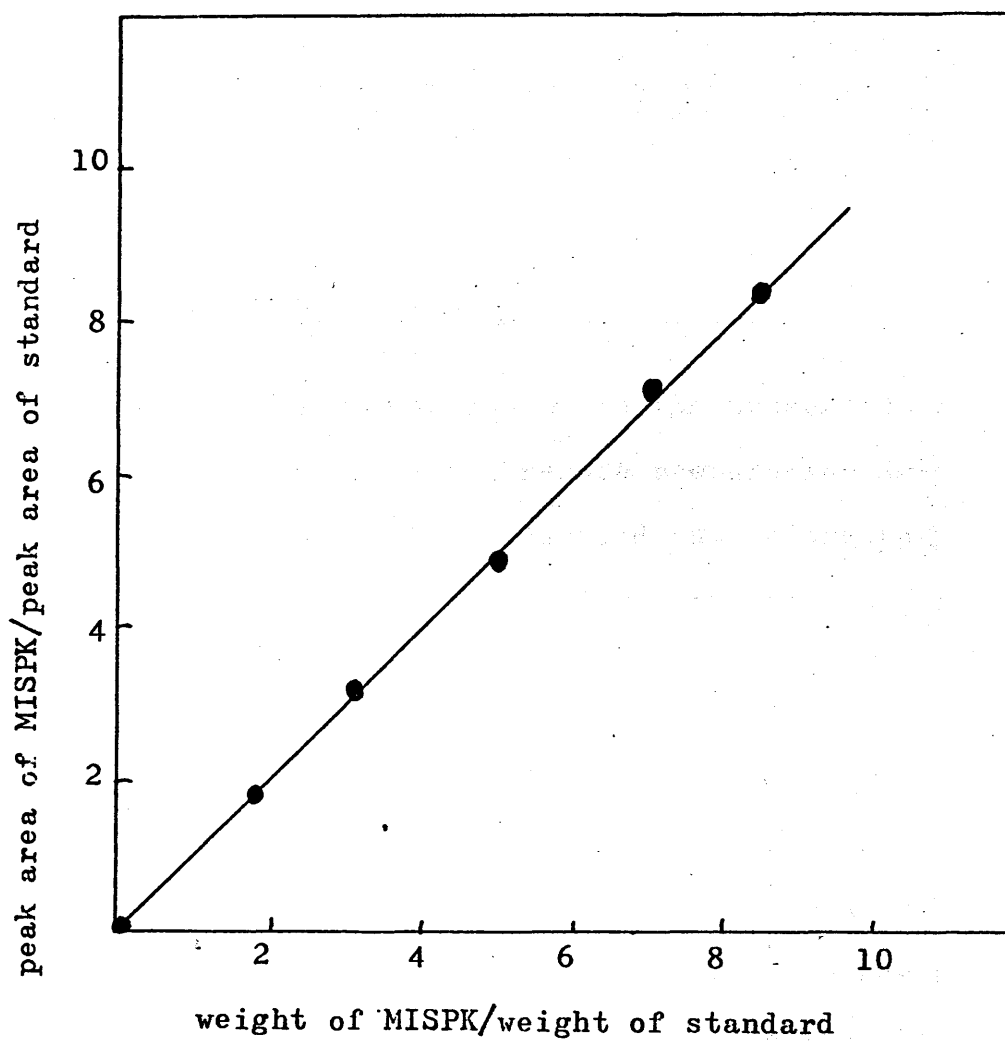


Fig. 2.13 Glc calibration curve for methyl isopropylketone (MISPK)

C H A P T E R T H R E E

MONOMER AND POLYMER PREPARATION

None of the monomers used in the present study are commercially available, therefore preparation and characterization had to be carried out before polymerization. In this chapter monomer and polymer preparation and characterization are described.

INTRODUCTION

Most research on methacrylic monomers has been centred on the ester and nitrile derivatives and to a lesser degree on the amide. A smaller amount of attention has been given to the salts of monovalent cations and to the bifunctional methacrylic monomers and polymers.

Solid state polymerization of alkali and alkaline earth metal salts of methacrylic acid has been studied by various workers.⁵⁶⁻⁵⁹ Polymerization in the solid state is now recognised to be possible for a wide variety of monomers, but there is little fundamental understanding of the process or even of the relative importance of chemical and physical parameters. Most of these solid state polymerization

investigations were undertaken to determine whether a crystalline polymer was formed.

The kinetics of methacrylic acid polymerization in aqueous solution have been studied by various workers⁶⁰⁻⁶⁵ from low pH to values as high as pH 12. Blauer found that the rate of polymerization of 0.2N methacrylic acid falls sharply as the pH increases above 2.5-5 and reaches a minimum between pH 6 and 7. This minimum rate of polymerization is approximately one-fifth of the rate at pH 4.. They also showed that above pH 7 the rate rises slowly and then levels off between pH 9 and 12 at a rate which is almost twice the minimum rate. None of the above investigations included the characterization of the homopolymer produced at higher pH.

Kikuchi et al³⁵ prepared alkali metal salts of methacrylic acid and studied the kinetics of aqueous polymerization of potassium methacrylate. They suggested that potassium methacrylate can easily be polymerized in aqueous solution with ammonium persulphate as initiator at pH 8.2 but did not characterize the homopolymer so obtained. They also showed that the rate of polymerization is, in the initial stage, proportional to the first power of the monomer concentration and also to the first power of the initiator (ammonium persulphate) concentration.

Polymerization of alkaline earth metal salts of methacrylic acid has not been studied to any extent. Hopkin,³⁶ however, has studied the polymerization of the alkaline earth metal salts of acrylic acid, but did not characterize the polymers.

In the present studies the metal salts lithium methacrylate, sodium methacrylate, potassium methacrylate, caesium methacrylate, calcium methacrylate, barium methacrylate, strontium methacrylate, magnesium methacrylate and zinc methacrylate were synthesised and polymerized to the respective homopolymers. The polymers will be referred to as poly (lithium methacrylate), etc., abbreviated PLiMA etc., in the subsequent discussion.

PREPARATION OF THE MONOMERS

Several relatively simple processes may be employed to make the monomeric salts. Neutralization of methacrylic acid with the oxide, hydroxide or carbonate of the desired metal is the most direct method for preparing a variety of salts. With bases of sufficient strength, such as calcium hydroxide, saponification of methyl methacrylate is a convenient route. In the present investigations alkali metal salts of methacrylic acid were prepared by neutralizing the acid with the respective hydroxide in methanol and alkaline earth metal salts by neutralizing the acid with the corresponding oxide or hydroxide in water. The alkaline earth metal salts were not prepared in methanol or ethanol because of their low solubility in non-aqueous solvents. Therefore two typical methods for preparing the salts in aqueous and non-aqueous media, respectively, will be described in detail.

DISTILLATION OF METHACRYLIC ACID

Methacrylic acid (Koch-Light) was purified by distillation under reduced pressure (20 mm Hg) at 70°C using 0.1% hydroquinone as inhibitor and with addition of a few boiling stones to avoid bumping. Only the middle fraction was collected for experimental use.

PREPARATION OF ALKALI METAL (Li, Na, K and Cs) SALTS:-

20 g of the appropriate hydroxide (A.R) were dissolved in 100 ml of methanol (A.R) and the solution was cooled in an ice bath. This alkali solution was neutralized with freshly distilled methacrylic acid using phenolphthalein as indicator. The stoichiometric amount of methacrylic acid was added dropwise and the temperature of the solution was maintained between 10°C and 15°C during the whole course of neutralization. These two precautions are very important as the bulk addition of the acid to the alkali solution produces sufficient heat of neutralization to result in the polymerization of the unsaturated acid. The neutralized solution was filtered and then gradually poured into one litre of anhydrous diethyl-ether (A.R) with constant stirring. The white precipitate of the metal salt was filtered, washed with ether twice and then with acetone (A.R). The salt was further purified by redissolving it in methanol and reprecipitating in anhydrous ether. The monomer was dried under vacuum at room temperature for 24 hours before subsequent analysis or polymerization.

PREPARATION OF ALKALINE EARTH METAL SALTS:-

The solid hydroxide or oxide of the desired divalent metal was added in small amounts, with vigorous stirring, to an approximately 3N aqueous solution of freshly distilled methacrylic acid. The temperature of the solution was maintained between 10°C and 15°C by cooling it in an ice bath from time to time. At the phenolphthalein end point a slight excess of methacrylic acid was added and the solution was filtered to remove the undissolved material. The filtrate was poured into an excess of acetone (A.R) and the white precipitate was filtered and washed twice with acetone. The monomer was further purified, by redissolving and reprecipitating. The salt was dried under vacuum at room temperature.

As previously noted, divalent salts were prepared in water, because of their low solubility in methanol or ethanol. The only exception was zinc methacrylate, which is even more soluble in methanol than are the monovalent metal salts. However, unlike the alkali metal salts, zinc methacrylate monomer cannot be isolated from methanol solution by direct precipitation with common non-polar solvents, such as benzene, ether, toluene etc. The salt was therefore obtained by crystallization.

CHARACTERIZATION OF MONOMERS

If considered solely as conventional salts, these materials show a pattern of chemical behaviour analogous to such related salts as the acetates or propionates. Divalent metal salts are neutral and monovalent salts are alkaline. The existence of the double bond in the methacrylate metal salts accounts for the sharp contrast in chemical behaviour between these salts and those of the isobutyrate class.

Characterization of the monomers was carried out by three different routes: (a) C, H, analysis, (b) estimation of metal contents by gravimetric analysis, volumetric analysis and by flame photometry, (c) infra red spectroscopic investigation for double bond and carbonyl frequencies.

(a) C, H analysis

Thermogravimetric analysis was carried out, before the elementary analysis of the monomers, in order to determine the absorbed moisture. The results obtained from microanalysis were then corrected for the amount of water present in the sample. The percentages of hydrogen were not reproducible, therefore these are stated as obtained from the analysis. The results for the anhydrous salts are listed in Table 3.2.

(b) Metal contents⁶⁶

Sodium and potassium methacrylate were analysed by flame photometry. Lithium, caesium and magnesium were determined gravimetrically and calcium, strontium and zinc were determined volumetrically. The details of the methods employed are given below:

Determination of lithium: 0.1-0.2 g of the anhydrous powdered sample was weighed into a porcelain crucible and treated with a few drops of concentrated sulphuric acid. The crucible was covered, placed in an inclined position and heated by directing the flame against the cover of the crucible. As soon as the thick white fumes of sulphuric acid began to diminish in quantity, the flame was moved towards the base of the crucible and finally the crucible was heated to dull red heat until the fumes were driven off. It was then removed from the flame, cooled in a dessicator to room temperature and weighed. The process of ignition and weighing was repeated until a constant weight within 0.1% difference was obtained. The percentage of lithium in the sample can be calculated as follows:-

Li_2SO_4 contains 12.61% lithium

$$\text{therefore \%age of Li} = \frac{\text{wt. of precipitate } (\text{Li}_2\text{SO}_4)(\text{g}) \times 12.61}{\text{wt. of sample (g)}}$$

Determination of caesium: An accurately weighed sample of caesium methacrylate of between 0.2 and 0.3 g in a porcelain evaporating dish was ignited in the presence of a few drops of concentrated hydrochloric acid to remove the organic part of the sample. The white solid mass thus obtained was treated with 3 ml of 60% perchloric acid and evaporated on the hot plate at a temperature about 250°C for half an hour. Addition of 0.02 ml of perchloric acid and evaporation was repeated twice in order to ensure the conversion of Cs^+ to caesium perchlorate. The resulting precipitate was dried under vacuum at 70°C for two hours and then heated at a

temperature about 300°C on the hot plate for half an hour. The crucible was cooled to room temperature in a dessicator. The determination was conducted in triplicate.

CALCULATION

CsClO_4 contains 64.42% of Cs, therefore the percentage of Cs in the sample can be calculated by the following equation:

$$\% \text{ Cs} = \frac{\text{wt. of precipitate (g)}}{\text{wt. of sample (g)}} \times 64.42$$

Determination of sodium and potassium. (Flame photometry)

In this technique solutions of known or unknown concentrations of a salt are sprayed into the Flame Photometer, but as the polymer samples give viscous solutions, the alkali methacrylate samples were first converted into their corresponding metal halides as follows: 0.0235 g of sodium methacrylate and 0.2 g of potassium methacrylate were accurately weighed into two different porcelain evaporating dishes and heated in an oven at 700°C to obtain the respective oxide and remove the organic part of the sample. The oxides were each transferred into a 100 ml graduated flask along with a few drops of hydrochloric acid and the solutions were made up to 100 ml with deionized water.

Solutions of known concentrations of K^+ and Na^+ from their halides (KCl, NaCl A.R) were made as 10, 5, 2.5 and 1.0 parts per million. Samples of these were sprayed into the Flame Photometer (Evan's Electroselinium) and galvanometer readings

were taken using the respective filter. Calibration curves were prepared by plotting the galvanometer reading against the concentration, which gave a straight line in both cases. The concentration of unknown solution for analysis could then be found using the flame photometer by comparing the galvanometer reading with the calibration curves and therefore the percentage of sodium and potassium could be calculated.

Determination of Ca, Sr, Zn and Mg (EDTA Titrimetry).

Monomer and polymer samples (Table 3.1) of the corresponding metal were accurately weighed into porcelain evaporating dishes and heated in an oven at 700°C to destroy the organic part of the samples. The white residue so obtained was transferred into a pyrex flask along with 10 ml of HCl and 2 ml of concentrated HNO_3 and digested at 500°C . To the test solution (except in the case of zinc) 5.0 g of ammonium chloride (A.R) and 20.0 ml of ammonia solution were added and the solution was then diluted to about 50 ml with distilled water. A few drops of Eriochrome Black T as indicator were added and the solution was titrated against 0.1 EDTA until the colour changed from wine-red to blue.

Determination of zinc. Zinc ion solution obtained as above after ignition of the monomer sample, was diluted to about 75 ml with distilled water and three drops of indicator (xylenol orange) were added. Powdered hexamine was agitated into the yellow solution until it acquired an intense red colour, it was then titrated with standard 0.05 M EDTA until the colour change from red to yellow occurred.

The mean values of EDTA used against the amount of samples and type of indicator, are summarized in Table 3.1. The weight of the various divalent cations present can be calculated from EDTA titration data using the following equations:-

(a) 1 ml of 0.1 M EDTA = 4.008 mg Ca

(b) 1 ml of 0.1 M EDTA = 8.763 mg Sr

(c) 1 ml of 0.05 M EDTA = 3.269 mg Zn

(d) 1 ml of 0.1 M EDTA = 2.432 mg Mg

Determination of barium. (Gravimetrically). An accurately weighed 0.3134 g sample of barium methacrylate in a porcelain evaporating dish was strongly ignited to burn the carbon contents. Addition of dilute sulphuric acid and ignition was repeated three times and the white mass so obtained was cooled to room temperature in a dessicator and weighed.

The percentage of barium calculated as:-

BaSO_4 contains 58.84% of Ba

therefore in the sample,

$$\% \text{ Ba} = \frac{\text{wt. of precipitate (g)}}{\text{wt. of sample (g)}} \times 58.84$$

(c) Infra red spectroscopy of monomers

The IR spectra were obtained by the KBr disc technique using 1 - 2 mg of monomer or polymer and 300 mg of KBr.

The C=O stretching frequency in methacrylic acid is at 1700 cm^{-1} and C=C at 1645 cm^{-1} but in the case of the monomer salt the C=O frequency is shifted to lower wavenumbers by 130 cm^{-1} with almost unchanged C=C frequency. In the case of

divalent metal salts, the C=O absorption is broad, ranging from 1600-1530 cm^{-1} , but again the double bond is unchanged at 1640 cm^{-1} .

The C=O and C=C frequencies for the various salts are summarized in Table 3.3 and a comparison of the spectra of methacrylic acid and its monovalent and divalent salts is shown in Fig. 3.1.

| Methacrylates | Wt. of dry sample (g) | Conc. of EDTA | Indicator | Vol. of EDTA used (ml) |
|---------------|-----------------------|---------------|--------------------|------------------------|
| CaMA | 0.2214 | 0.1 M | Eriochrome-black T | 10.2 |
| CaPMA | 0.3156 | 0.1 M | | 14.5 |
| SrMA | 0.1560 | 0.1 M | Eriochrome-black T | 5.9 |
| SrPMA | 0.2121 | 0.1 M | | 7.2 |
| ZnMA | 0.2944 | 0.05 M | Xylenol-orange | 24.5 |
| ZnPMA | 0.2561 | 0.05 M | | 21.2 |
| MgMA | 0.1875 | 0.1 M | Eriochrome-black T | 9.5 |
| MgPMA | 0.2312 | 0.1 M | | 11.5 |

Table 3.1

EDTA Titration Data

| Methacrylate | Calculated | | Observed | | % Metal Contents | |
|--------------|------------|------|----------|------|------------------|----------|
| | %C | %H | %C | %H | Calculated | Observed |
| LiMA | 52.09 | 5.47 | 52.51 | 5.51 | 7.53 | 7.60 |
| NaMA | 44.44 | 4.62 | 44.14 | 4.74 | 21.29 | 21.36 |
| KMA | 37.77 | 4.03 | 37.75 | 4.1 | 31.42 | 31.5 |
| CsMA | 23.23 | 1.96 | 22.51 | 2.01 | 60.99 | 60.90 |
| CaMA | 45.67 | 4.79 | 45.63 | 4.95 | 19.07 | 18.46 |
| BaMA | 31.22 | 3.20 | 30.95 | 3.85 | 44.67 | 44.52 |
| SrMA | 37.25 | 3.91 | 38.8 | 4.23 | 34.0 | 33.14 |
| MgMA | 49.89 | 5.23 | 49.75 | 5.64 | 12.64 | 12.32 |
| ZnMA | 40.77 | 4.28 | 40.71 | 4.32 | 27.76 | 27.20 |

Table 3.2

Analytical Data Of Monomers

| Methacrylate | C=O cm^{-1} | C=C cm^{-1} |
|--------------|----------------------|----------------------|
| MAA (acid) | 1700 | 1640 |
| LiMA | 1560 | 1645 |
| NaMA | 1550 | 1640 |
| KMA | 1555 | 1640 |
| CsMA | 1560 | 1645 |
| CaMA | 1560-1570 (broad) | 1650 |
| BaMA | 1560-1570 (") | 1650 |
| SrMA | 1555-1575 (") | 1650 |
| MgMA | 1550-1590 (") | 1650 |
| ZnMA | 1510-1610 (") | 1660 |

Table 3.3

C=O and C=C Frequencies for the Various Salts.

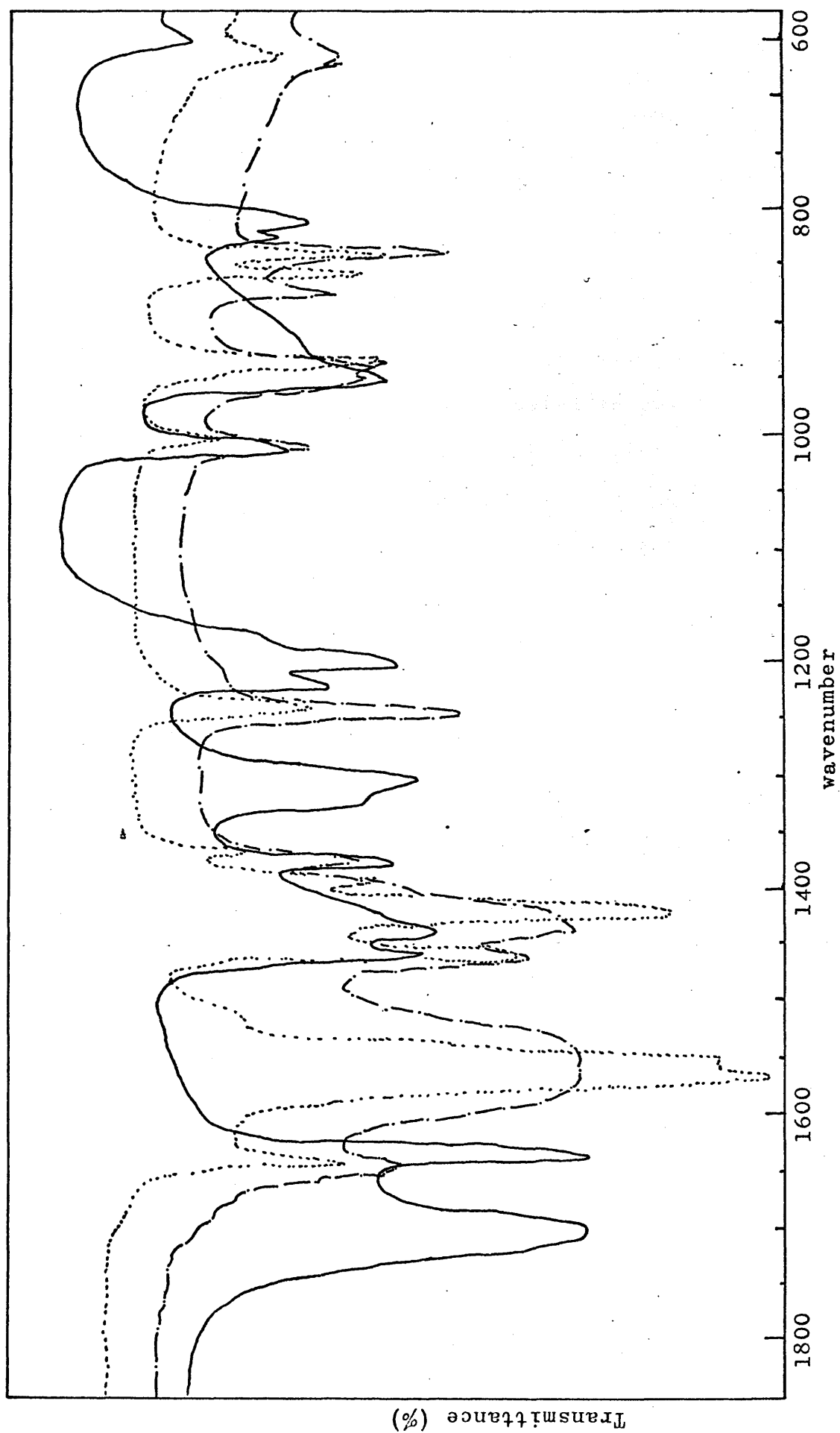


Fig. 3.1 IR absorption spectra of monomers; — MAA, - - - CaMA and KMA

POLYMERIZATION

The monomers are solids, therefore the homopolymers were obtained by solution polymerization. The solution polymerization of the monomer salts was carried out by the following two different routes.

- (a) Aqueous polymerization under nitrogen.
- (b) Methanol solution polymerization under vacuum.

Aqueous polymerization can be applied to all monomer salts of methacrylic acid, but methanol solution polymerization is limited to lithium, sodium, potassium, caesium and zinc methacrylates, because of their reasonable solubility in methanol while the other monomers are less than 1% soluble. During the investigation of the aqueous polymerization of alkali metal methacrylates, it was found that if the pH of the solution is not raised by an additional amount of alkali, there results a copolymer of the acid and its monomer salt instead of the starting monomer. The variation of temperature, monomer and initiator concentration did not help to produce a homopolymer. The production of the copolymer instead of a homopolymer is obviously the result of hydrolysis of the salt of the weak acid and strong alkali. But this salt hydrolysis was insignificant in the case of divalent methacrylates, since the infra-red spectra of the divalent metal polymethacrylates obtained did not show any absorption at 1700 cm^{-1} , which is assigned to the C=O stretching frequency of the acid unit.

In the present investigation, it was found that alkali metal methacrylates are more soluble than alkaline earth metal

methacrylates. The solubility of monovalent metal methacrylate was found to be as high as 40% weight by volume of water at room temperature and it increases with the size of ion. On the other hand, the divalent metal salts show much lower solubility in water (8% weight by volume) at room temperature. The solubility increases to 25% at 60°C, but does not vary markedly with the size of the metal ion as in the case of the alkali metal methacrylate salts. As noted earlier, alkali metal methacrylates give alkaline solutions in water while the alkaline earth metal methacrylates give neutral solutions. In the case of divalent metal salts, there could be the formation of complex intramolecular structures involving pairs of carboxyl groups associated with the metal ion. Cotton and Wilkinson⁶⁷ have pointed out that in aqueous solutions of M^{2+} ions, the ions are not at all hydrolysed, but weak complexes can be formed by the lighter group II elements. The interaction of polyelectrolytes and their counterions has been the subject of much experimental and theoretical work. The complexing of linear poly-ions with strongly complexing ions has been studied by Morawetz, Gregor, Wall and their co-workers.⁶⁸ Morawetz et al,⁶⁹ determined the complex formation constant for alkaline earth metal ions with a maleic acid copolymer and assumed that a chelate involving two neighbouring carboxyl groups was the only type of complex formed. They also found a titration shift and interpreted it in terms of the extent of counterion binding. The binding of Cu^{++} to polyacrylic and polymethacrylic acids, has been investigated by Kotliar and Morawetz,⁷⁰ Wall and Gill,⁷¹ and Gregor et al⁷² and they all

agree that the high affinity of the polyions for Cu^{++} leaves no doubts that chelate formation must be involved. The co-operation of two neighbouring carboxylates would, however, result in eight-membered rings which are known to form with great difficulty and larger rings involving carboxylates at greater distances along the polymeric chain must account for most of the cation binding. The data of Fronaeus⁷³ on the binding of acetate by Cu^{++} also makes it clear that the possibility of binding with more than two carboxylate groups cannot be disregarded when a Cu^{++} ion finds itself surrounded by the high local concentration of carboxylate in the region occupied by polyions, but this situation is not relevant to the present studies because the stoichiometric amounts of carboxylate anion and cation were present throughout the reaction. Mandel and Leyte⁷⁴ studied the interaction of bivalent ions of Cu, Cd, Zn, Ni, Co and Mg with poly (methacrylic acid) and from the titration curves obtained, suggested that these metals seemed to form complexes involving two carboxylate groups for each ion over a large pH range. Site binding also occurs in monovalent salts of polyacids. From transference experiments, Noll and Gill⁷⁵ concluded that Cs^+ ions are much less bound by polyacrylic acid than Na^+ ions. As a result of ion binding in monovalent salts, a higher pH was required during the polymerization of potassium and caesium methacrylates as shown in Table 3.4. The raising of the pH of the solution

in the aqueous polymerization of alkali metal salts was carried out by using the respective alkali, not by use of buffer solutions to avoid any complication due to further ionic species in the reaction mixture. The alkaline earth metal methacrylates were polymerized in neutral aqueous solution.

Aqueous polymerization. Monomer and initiator concentrations, temperature and pH employed are summarized in Tables 3.4 and 3.5. The general method used for aqueous polymerization is described below.

The monomer salt dissolved in an aqueous solution of the desired base was transferred into a three neck flask, fitted with a condenser, inlet for nitrogen stream and a thermometer. The flask was immersed in a thermostat at the required temperature and a vigorous stream of oxygen free nitrogen was flushed through the reaction mixture for 45 minutes to bubble out all the dissolved oxygen. Initiator was introduced through the third inlet and after a considerable time the reaction vessel was removed from the thermostat, the viscous solution was poured into methanol and the rubbery, sticky white mass which precipitated was filtered and washed with methanol three times. The polymer was dried under vacuum for 24 hours, ground to a fine powder and again washed with hot methanol three times. The polymer was dried under vacuum at 70°C for 36 hours.

| Methacrylate | wt. of monomer (g) | H ₂ O (ml) | pH | Initiator (ml) $\frac{v}{v_s}$ 90% H ₂ O ₂ | Time (HRS) | Yield % |
|--------------|--------------------|-----------------------|------|--|------------|---------|
| LiMA | 30.5 | 70 | 10.1 | 0.07 | 8 | 20.5 |
| NaMA | 35.5929 | 75 | 10.5 | 0.075 | 7.5 | 18.2 |
| KMA | 40.3498 | 100 | 11.1 | 0.1 | 9 | 19.9 |
| CsMA | 25.2310 | 60 | 11.5 | 0.06 | 6 | 16.5 |

Table 3.4

Alkali metal methacrylates polymerization data,
temperature 40°C, initiator = 90% H₂O₂ 0.1% v/v

| Methacrylate | wt. of monomer (g) | H ₂ O (solvent) (ml) | Initiator w/v _s (NH ₄) ₂ S ₂ O ₈ | Time (HRS) | Yield % |
|--------------|--------------------|---------------------------------|--|------------|---------|
| CaMA | 30.512 | 100 | 0.05 gms | 1.15 | 16.3 |
| BaMA | 25.6742 | 80 | 0.04 gms | 1.20 | 16.5 |
| SrMA | 35.2321 | 100 | 0.05 gms | 1.30 | 20.3 |
| MgMA | 37.576 | 100 | 0.05 gms | 1.30 | 21.5 |
| ZnMA | 40.2376 | 80 | 0.04 gms | 2.00 | 20.4 |

Table 3.5

Divalent metal methacrylates, polymerization data,
 temperature = 60°C, initiator = (NH₄)₂S₂O₈, 0.05% w/v.

The divalent methacrylates were polymerized in a similar way except for the use of higher temperature, different initiator and neutral solutions. The homopolymers are insoluble in water and were purified by successive washing with distilled water to remove monomer. They were dried under vacuum at 70°C for at least 60 hours, since it is difficult to remove the water which is present. After this long drying, they were found to be anhydrous and less hygroscopic than the monovalent salts.

METHANOL SOLUTION POLYMERIZATION

The alkali metal salts studied were polymerized in methanol in a sealed vacuum system and since this is a new method for synthesizing these polymers, the preparation is described in detail.

Polymerizations were carried out in 100 ml dilatometers. They were washed with cleaning fluid, distilled water, analar acetone and dried by pumping to high vacuum. They were flamed out to remove any volatiles adsorbed on the glass.

Purification of initiator. In all these polymerizations azo-di-isobutyronitrile (AIBN (Kodak Ltd) was used as initiator. It was recrystallized from methanol (Analar) and added to the dilatometer as a standard solution in benzene. The benzene was removed under vacuum.

Purification of solvent. Methanol was chosen as a solvent because of the considerable solubility of these monomers in it.

The solubility of the alkali metal methacrylates was in the range of 8 - 10g in methanol at room temperature. Methanol was purified by treatment for 24 hours with dried calcium chloride, then overnight with ground calcium hydride to remove all traces of moisture. It was degassed by the usual freezing and thawing technique and distilled under vacuum into a graduated reservoir. Only the middle fraction of this distillate was used as solvent.

Introduction of monomer and solvent into dilatometer. As the monomers were solids, they were introduced directly into the dilatometer through a funnel. Any monomer sticking to the surface of the tube was washed to the bottom of the dilatometer with a few ml of dried and distilled methanol which was then pumped off under high vacuum. After the dilatometer had been pumped to a pressure of 10^{-5} torr, solvent was introduced, in all cases by distillation under vacuum from a graduated reservoir. Once the polymerization mixture of initiator, monomer and solvent had been made up in the dilatometer, it was frozen with liquid nitrogen, pumped to a pressure of less than 10^{-5} torr and the dilatometer was then sealed.

Polymerization. All polymerizations were carried out at $60^{\circ} \pm 1^{\circ}\text{C}$ to not more than 20% conversion. After the required time, the dilatometer was removed from the thermostat and cooled in an ice bath. The polymer was removed by filtration and washed with dried methanol three times to obtain polymer free of monomer. It was dried under vacuum at 70°C for 48 hours and stored in an evacuated dessicator. The polymerization data for homopolymers is given in Table 3.6

| Polymer | Initiator conc. wt/vol | Monomer conc. w/v | Time (HRS) | wt. of polymer (g) | % conversion |
|---------|------------------------------|-------------------------|---------------|--------------------------|-----------------|
| LiPMA | 0.01% | 8.2131 | 3.5 | 1.2730 | 15.5 |
| NaPMA | 0.01% | 7.5421 | 3.0 | 0.9352 | 12.4 |
| KPMA | 0.01% | 8.8761 | 2.5 | 0.9053 | 10.2 |
| CsPMA | 0.01% | 9.1231 | 2.0 | 1.3501 | 14.7 |
| ZnPMA | 0.05% | 8.5421 | 1.5 | 1.4084 | 16.5 |

Table 3.6

Polymerization data for homopolymerization
in methanol.

POLYMER CHARACTERIZATION

Homopolymers were characterized in a manner similar to that for monomers. The only difficulty encountered in these polymer characterizations was that the homopolymers were found to be more hygroscopic than their respective monomers. Therefore before the analysis was performed the moisture contents were found by thermogravimetry. Analytical results obtained are summarised in Table 3.7.

The infra red spectra were obtained in the solid state using the KBr disc technique. An IR investigation of the salts of polymethacrylic acid has been made previously by Leyte and co-workers, who obtained the polymers by neutralizing the polyacid with the required base. The IR fundamentals obtained in the present studies were found to be in general agreement with those obtained by Leyte and co-workers.⁷⁶ In the spectra of the homopolymers the carbonyl symmetrical and antisymmetrical stretching were at the same frequencies as in the monomers, but the peaks for the double bond completely vanished. A band at 1245 cm^{-1} , present in monomer spectra, but absent in homopolymer spectra, was assigned by Leyte and co-workers to $\nu(\text{CO})$; this band was replaced by another fundamental at 1205 cm^{-1} . The infra red spectra of the homopolymers are not shown in this chapter but are included in Chapters 4 and 5 for comparison purposes.

| Polymer | Calculated | | Observed | | % Metal Contents | |
|---------|------------|------|----------|------|------------------|----------|
| | %C | %H | %C | %H | Calculated | Observed |
| PLiMA | 52.09 | 5.47 | 51.55 | 5.84 | 7.53 | 7.32 |
| PNaMA | 44.44 | 4.62 | 44.41 | 4.90 | 21.29 | 21.0 |
| PKMA | 37.77 | 4.03 | 37.92 | 4.83 | 31.42 | 31.0 |
| PCsMA | 23.23 | 1.96 | 22.05 | 2.32 | 60.99 | 60.01 |
| PCaMA | 45.67 | 4.79 | 44.14 | 4.89 | 19.07 | 19.3 |
| PBaMA | 31.22 | 3.20 | 30.14 | 3.75 | 44.67 | 43.95 |
| PSrMA | 37.25 | 3.91 | 38.8 | 4.23 | 34.0 | 33.51 |
| PMgMA | 49.89 | 5.23 | 48.95 | 5.80 | 12.64 | 12.81 |
| PZnMA | 40.77 | 4.28 | 39.70 | 4.79 | 27.76 | 28.12 |

Table 3.7

Analytical data of homopolymers

THERMAL STABILITY DATA OF MONOMERS

Thermal behaviour of calcium methacrylate has been studied by Furukawa and co-workers, who reported ten ketones. Their studies were based on the dry distillation of the salt at 450-500°C in an atmosphere of N_2 and did not specify the temperature at which the salt actually starts disintegrating. They have also pointed out that monomer salts at first were found to polymerize in the solid state before degradation, while the degree of polymerization was shown to be comparatively low. The thermal stability of the other monomer salts has not been studied in any detail in the past, therefore it was considered desirable to have a prior knowledge of their thermal degradation characteristics for comparison with their respective homopolymers. Thermal stability of the monomer salts was investigated by TVA and TGA.

Thermal volatilization analysis. The TVA curves obtained for all the nine monomer salts are shown in Fig. 3.2 to 3.10. In all cases the samples were degraded in the powder form up to 500°C at a rate of 10°C/min under normal TVA conditions. The sample sizes were between 50 to 60 mgs. It is clear from the TVA curves for alkali metal methacrylate that no volatile product is given off at temperature below 350°C. Above this temperature the sharp release of volatile material commences, including a non-condensable fraction. The area enclosed between the 0°C and -100°C, is

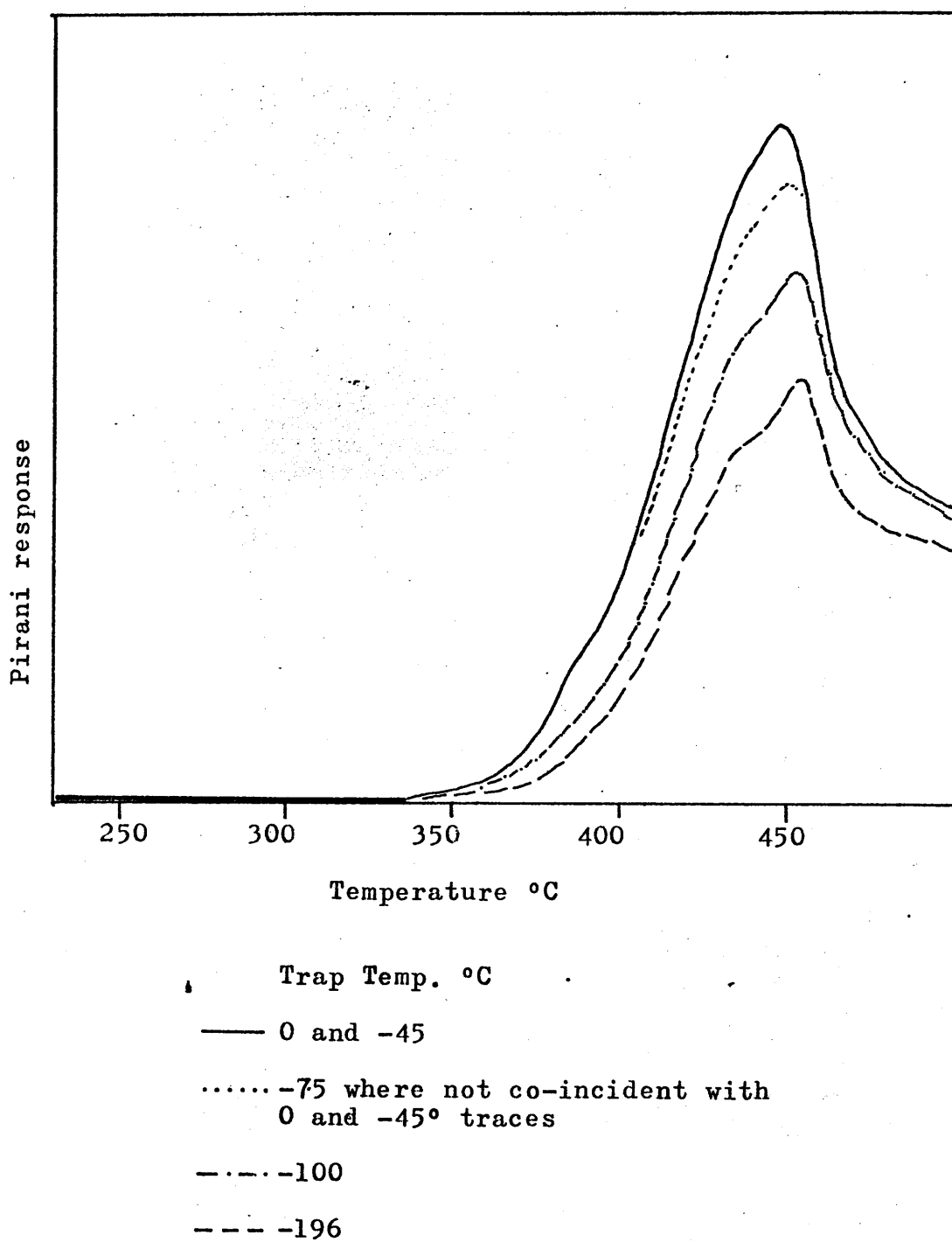


Fig. 3.2 TVA curve for lithium methacrylate

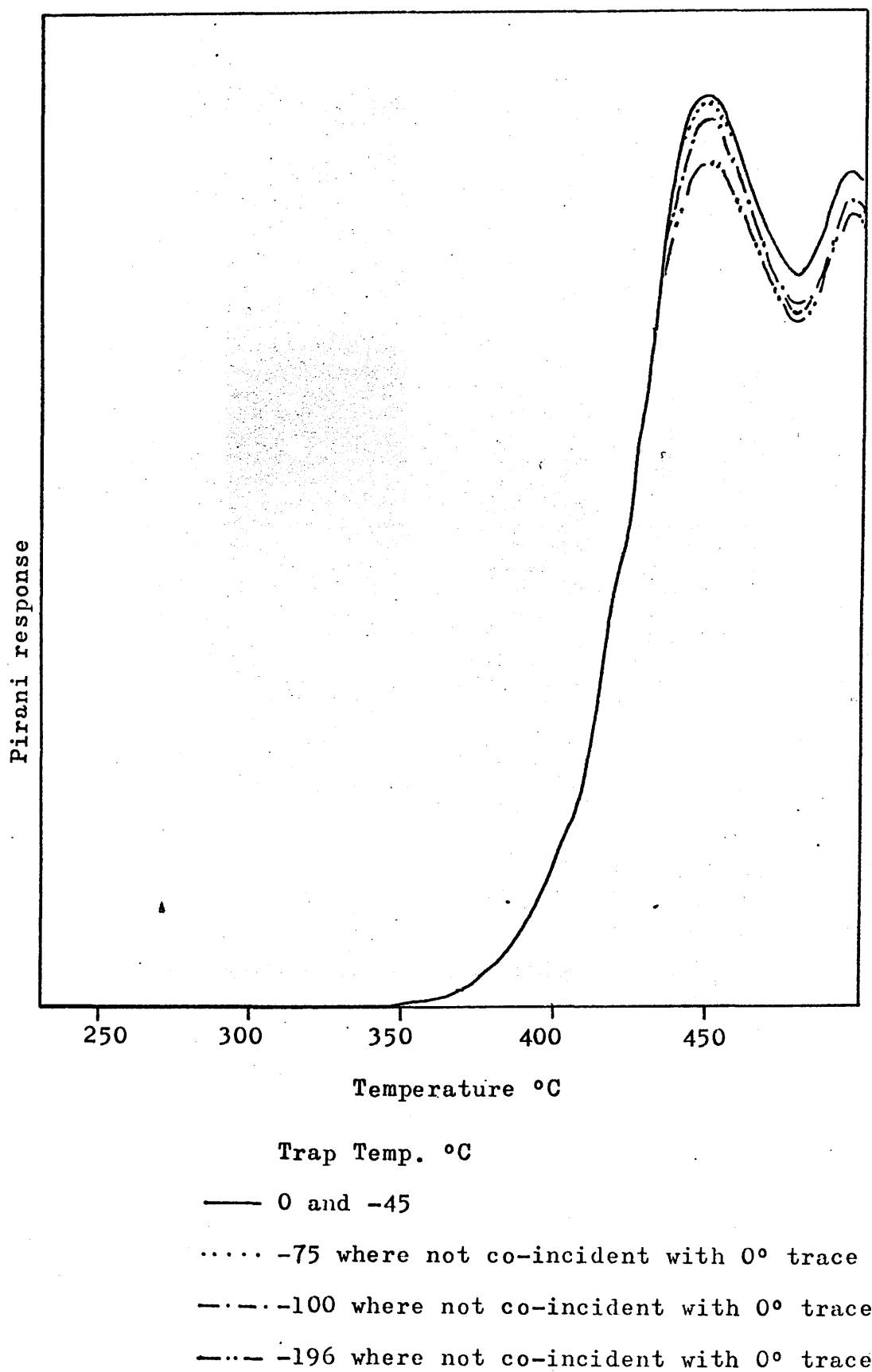


Fig. 3.3 TVA curve for sodium methacrylate

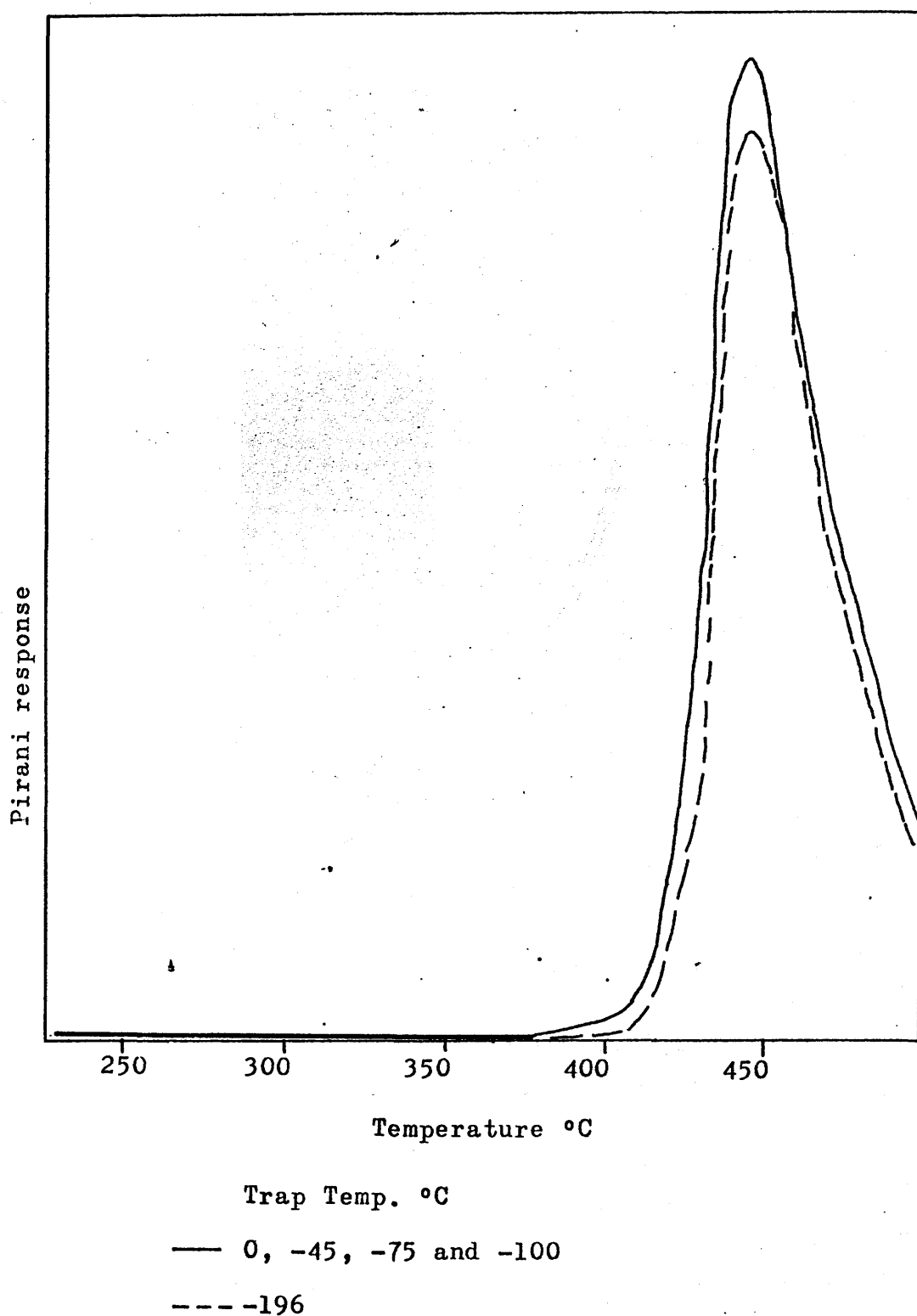


Fig. 3.4 TVA curve for potassium methacrylate

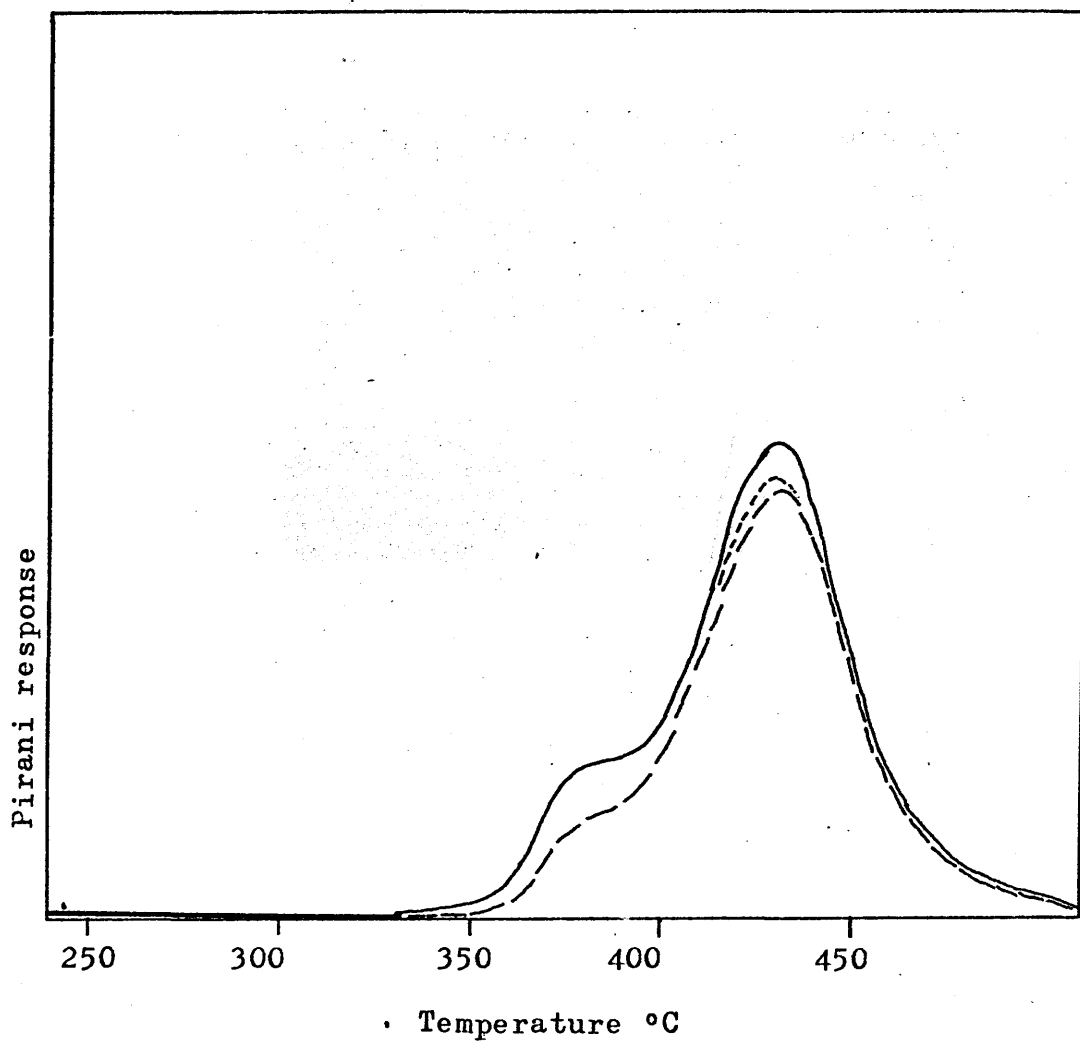


Fig. 3.5 TVA curve for caesium methacrylate

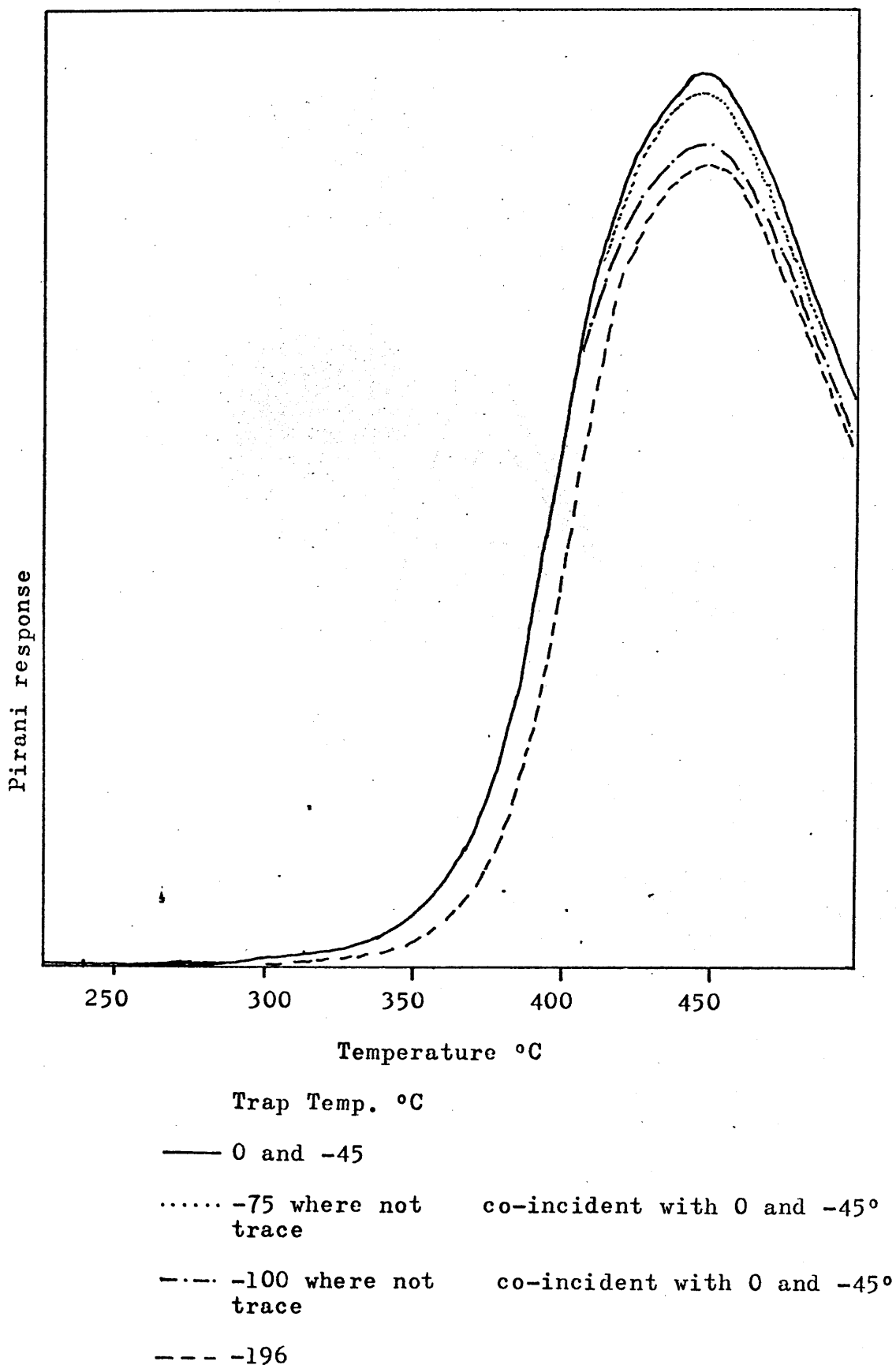


Fig. 3.6 TVA curve for zinc methacrylate

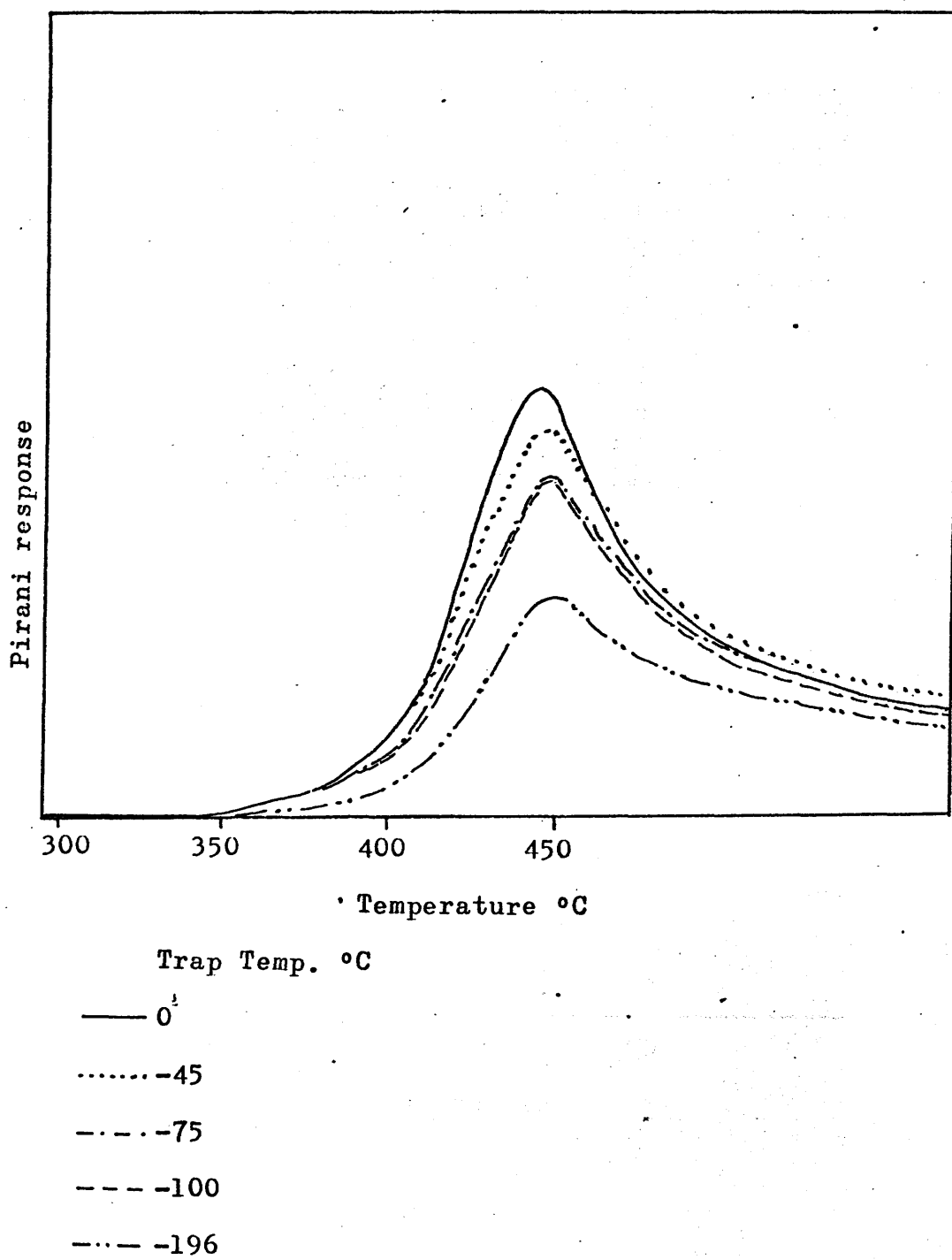
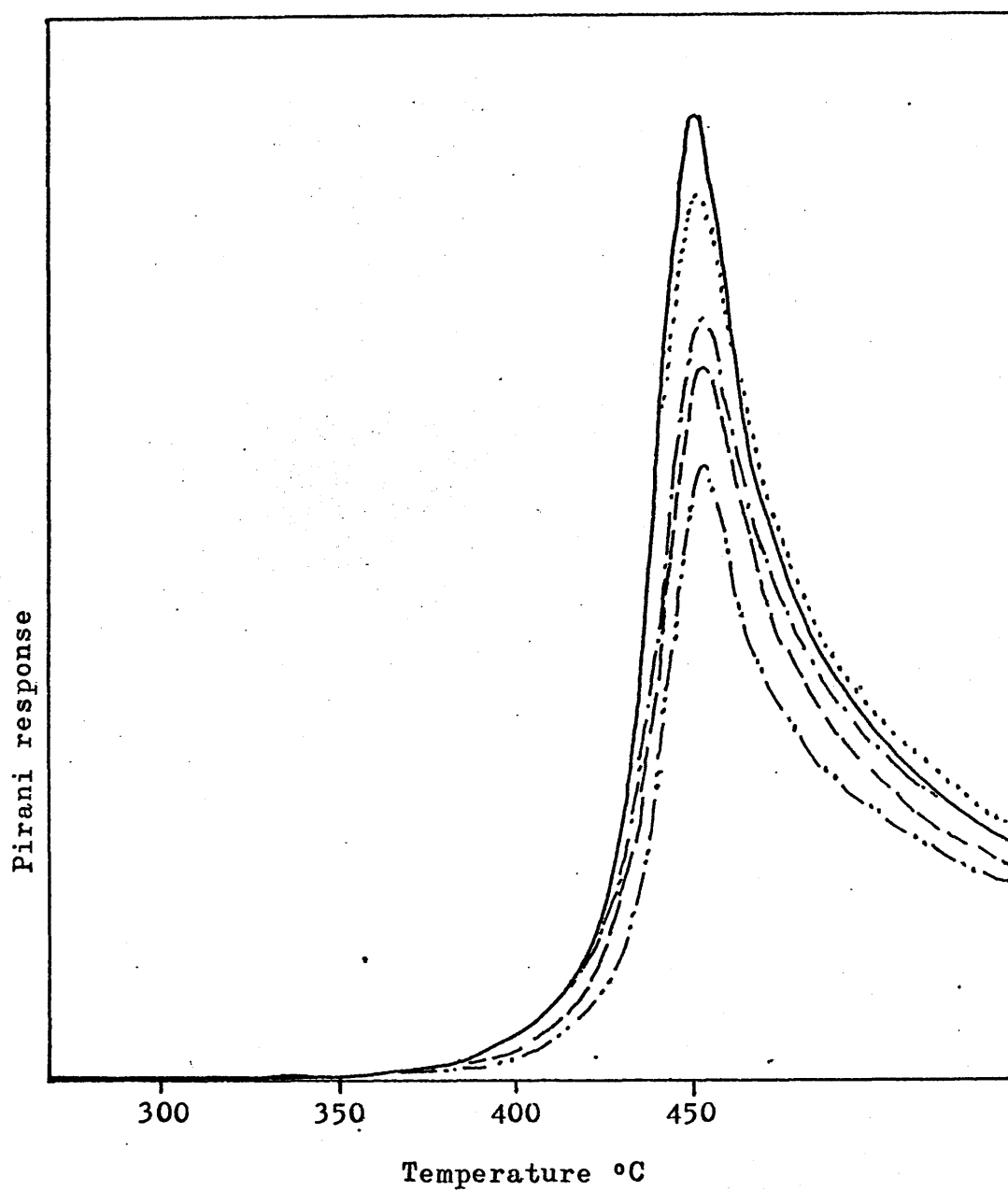


Fig. 3.7 TVA curve for magnesium methacrylate



Trap Temp. °C

— 0

..... -45

- - - - -75

- - - - -100

- · - · -196

Fig. 3.8 TVA curve for calcium methacrylate

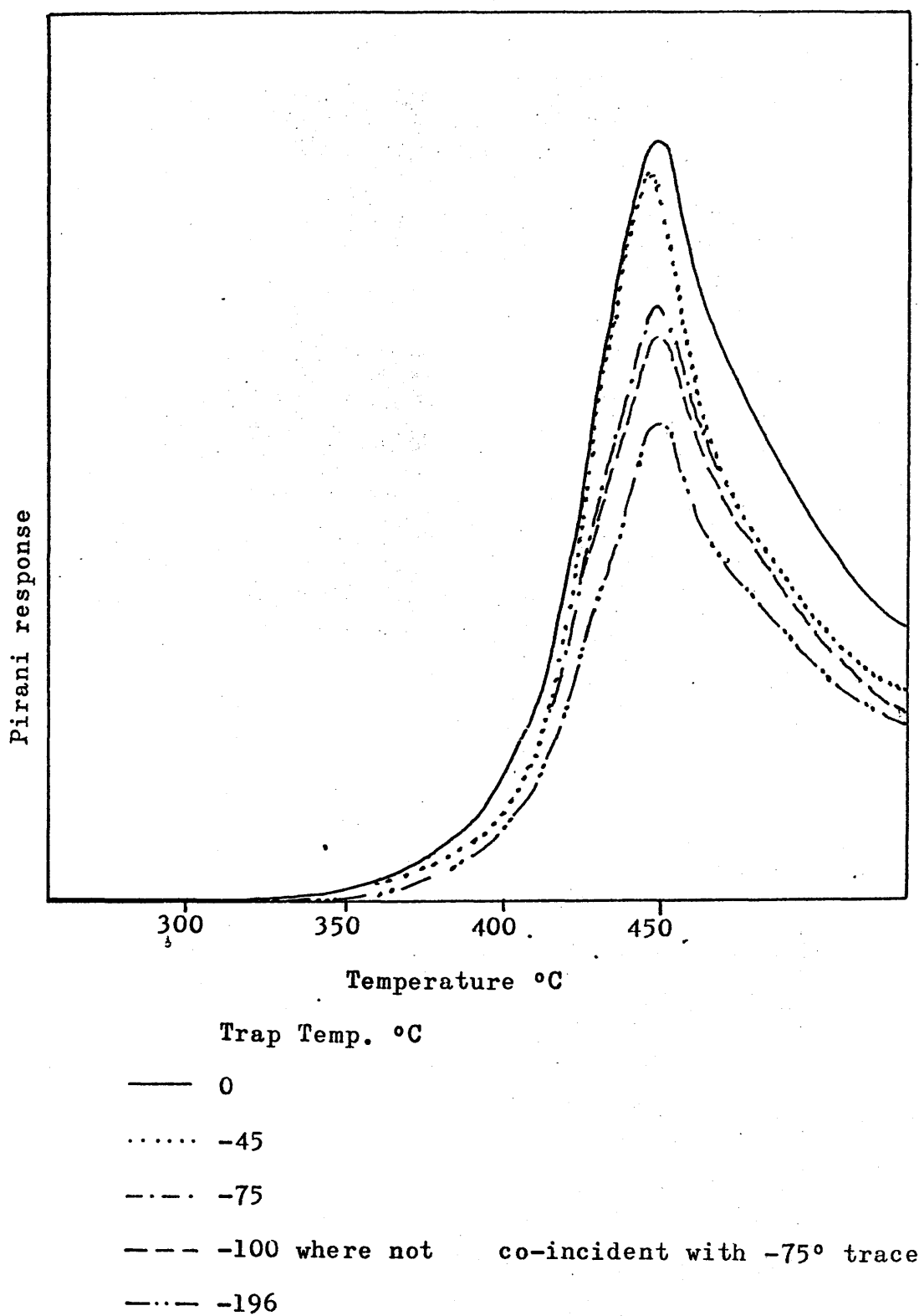


Fig. 3.9 TVA curve for strontium methacrylate

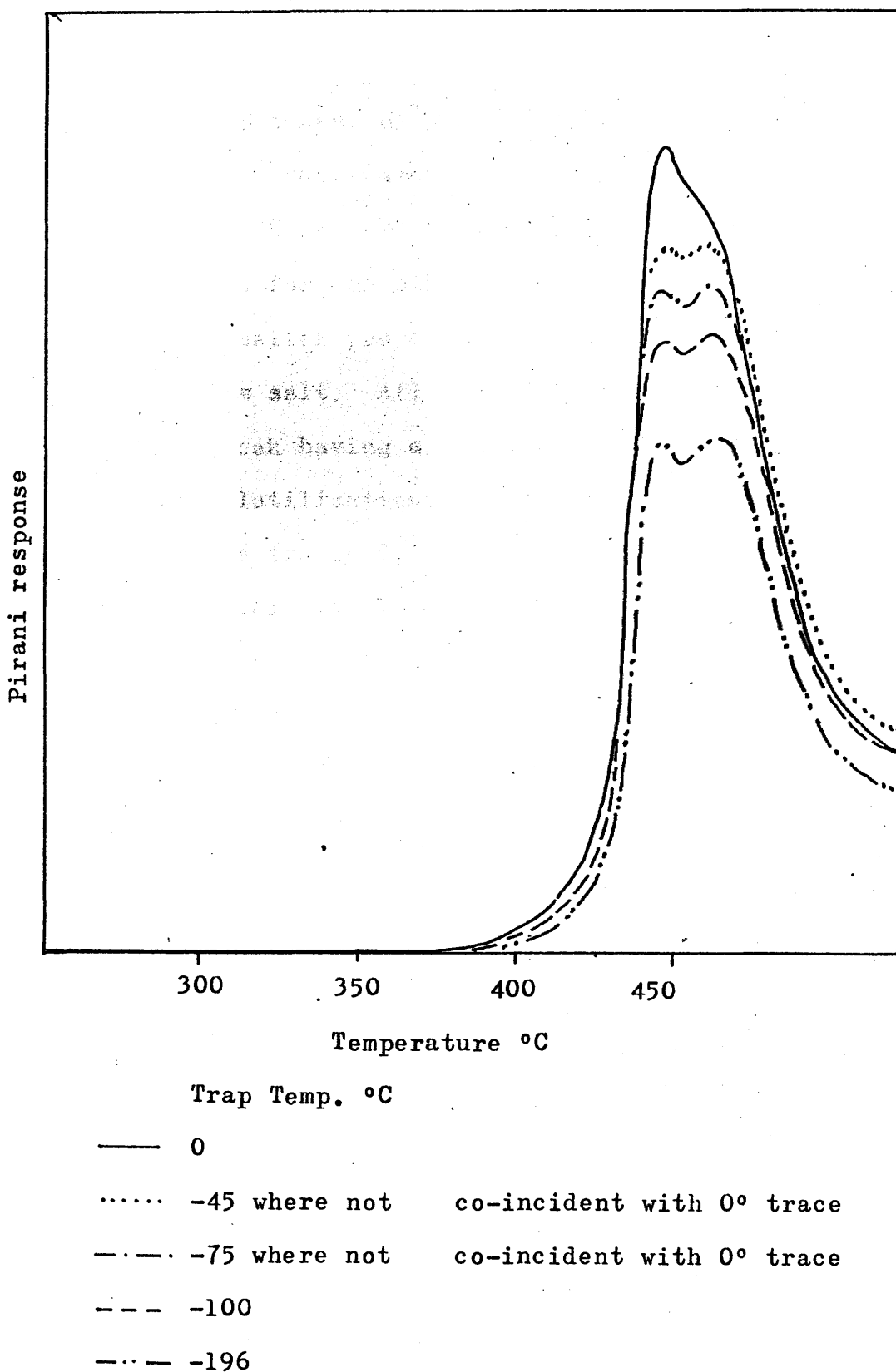


Fig. 3.10 TVA curve for barium methacrylate

very small in the case of NaMA, KMA and CsMA, indicating the presence of only small amounts of cyclic ketones. The separation of 0°C and -196°C traces in lithium methacrylate is greater than for the other alkali metal methacrylates, indicating a smaller proportion of non-condensable products for the lithium salt. All four TVA traces consist of a single broad peak having a T max (the temperature at which the rate of volatilization is maximum) around 440°C. After the T max's the traces 0, -45, -75, -100 and -196°C become coincidental; this may be due to the formation of carbon monoxide via secondary reaction.



The rate of the above reaction could be seen in the case of the NaMA thermogram, which gives another T max after the one at 420°C. In the divalent metal salts (except ZnMA) it is obvious that there is a considerable enclosed area between the 0°C and -100°C curves, which indicates the presence of cyclic ketones regardless of the size of the metal ion. The -45°C trace is well separated from the 0°C trace, but after the T max, it tends to cross the 0°C trace, indicating a limiting rate for some higher boiling cyclic ketones. The TVA curves for zinc methacrylate do not show the presence of large amounts of cyclic ketones, amongst the degradation products, but instead indicate non-condensables such as CO, CH₄. All these monomer salts give a single TVA peak and degrade more or less at the same temperature.

PRODUCT ANALYSIS

The terms used to describe the four kinds of products namely, non-condensables, condensables, 'cold-ring' and residue have been defined in Chapter 2. The condensable product analysis was carried out by distilling these into an infra red cell or into a capillary. The cold-ring products on the sides of the cooled upper part of the tube were analysed by IR spectroscopy using KBr discs. Residual material on the base of the TVA tube was identified in the same way. No attempt was made at quantitative measurement of the non-condensables.

IDENTIFICATION OF PRODUCTS

The volatile products from alkali metal methacrylates were, methane, isobutene, butene-1, ethylene, acetylene, benzene, toluene, carbon dioxide and carbon monoxide. They were identified by IR analysis. The liquid products were identified by IR analysis. The liquid products were identified by gas chromatography and were found to consist of dimethyl cyclopentanone, dimethyl cyclopentenone, methyl cyclopentanone, diethyl ketone, methyl ethyl ketone, methyl isopropyl ketone and traces of methyl-n-propenyl ketone and cyclopentanone. The volatile products obtained from divalent metal salts of methacrylic acid were similar, but larger amounts of cyclic ketones were obtained. Also CaMA, BaMA and

SrMA gave traces of dimethyl ketene, but MgMA and ZnMA gave dimethyl ketene as a major product. The typical spectra of volatile products obtained from CsMA, BaMA and MgMA are shown in Fig. 3.11 and a reference spectrum of dimethyl ketene is also included in the Figure.

On heating the monomer salts to 500°C, it was found that the cold-ring fraction for the alkali methacrylates consisted of monomer and metal isobutyrate, but the divalent metal methacrylates (except MgMA and ZnMA) gave no monomer or isobutyrate and the cold-ring fraction was negligible in amount. Magnesium methacrylate gave monomer while ZnMA produced zinc metal and zinc oxide. The IR spectra of cold-ring fractions from KMA and MgMA are shown in Fig. 3.12. The residue after degradation of the monomer salts to 500°C, was identified as a mixture of carbon and metal carbonates and metal oxides. In the case of the alkali metal methacrylates, no oxide was identified and zinc methacrylate gave no carbonate. The apparent absence of alkali metal oxides may be because of their readiness to form carbonate or bicarbonate on exposure to the atmosphere and the absence of carbonate in ZnMA is probably the result of the unstability of ZnCO_3 at 500°C.

Metal carbonate may form by elimination from adjacent salt groups as shown below - the resulting cyclobutanone structure rearranges by bond scission to give substituted cyclopentanones, which are then released:-

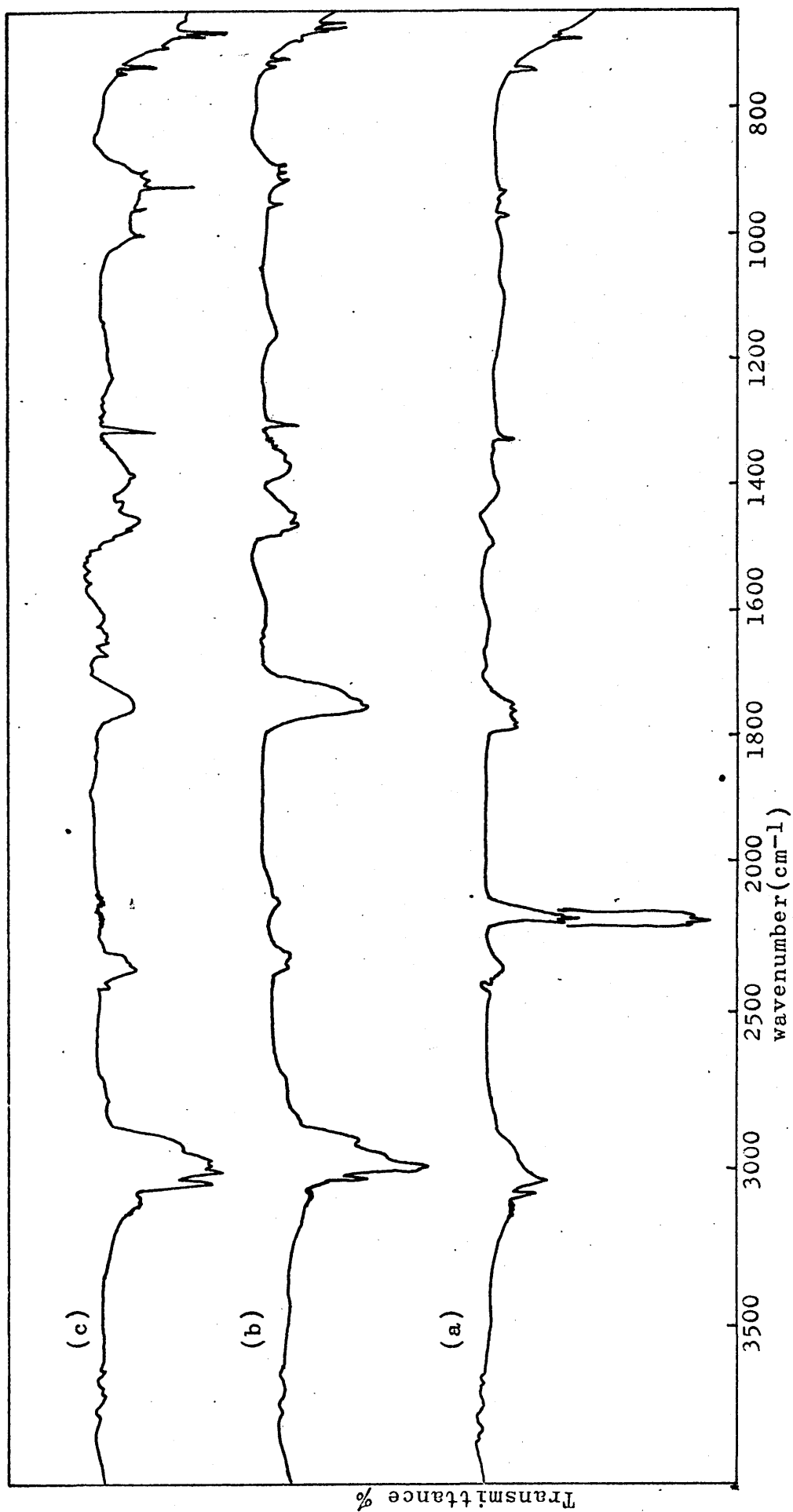


Fig. 3.11 IR spectrum of gaseous volatile products of; (a) CsMA, (b) BaMA and (c) MgMA

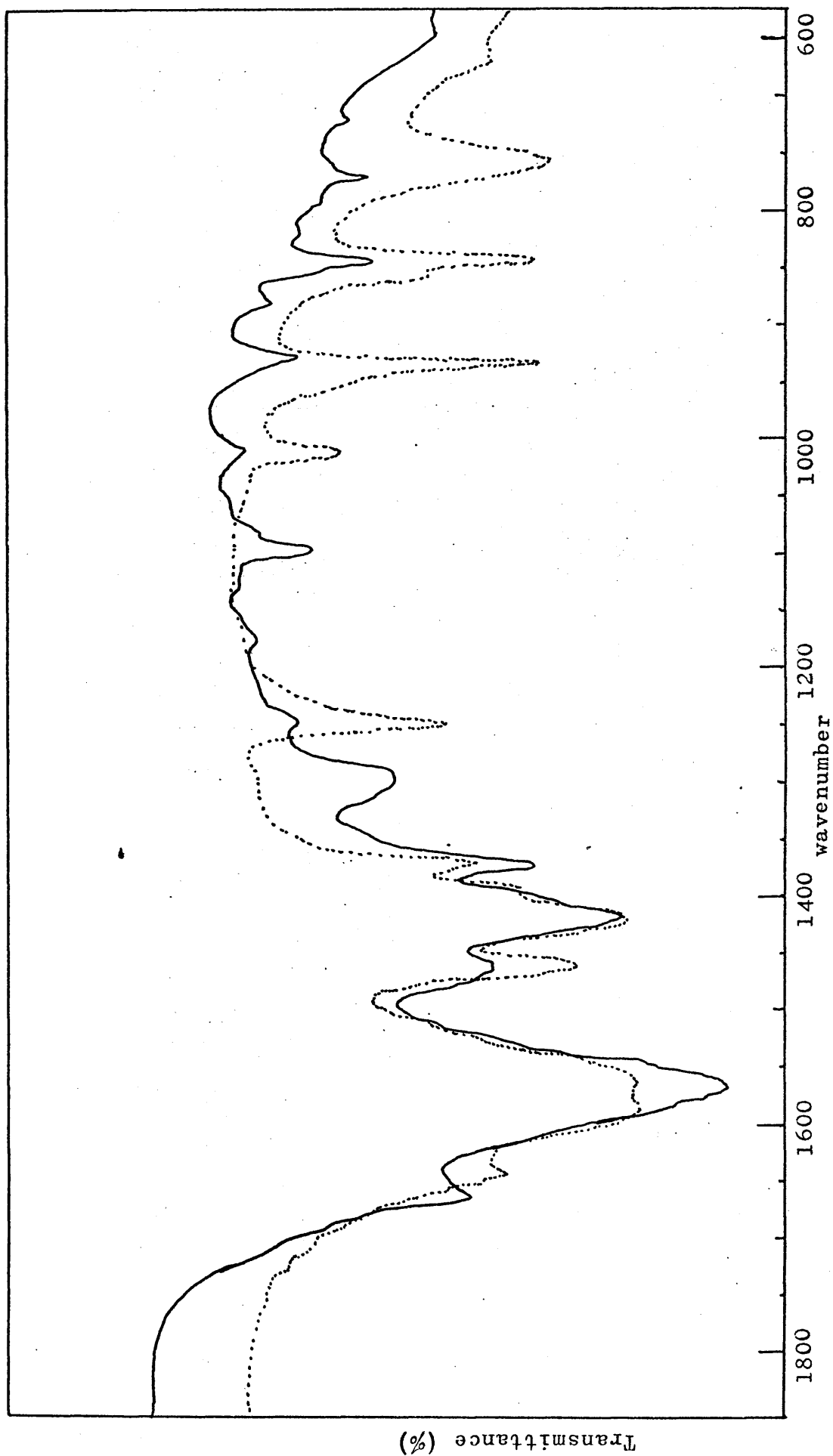
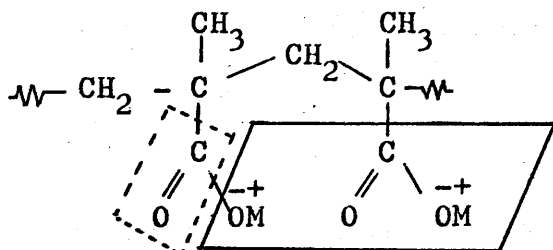


Fig. 3.12 IR absorption spectra of CRF from: — KMA and MgMA

| Monomer | % wt. loss at temperature | | |
|---------|---------------------------|-------|-------|
| | 300°C | 400°C | 500°C |
| LiMA | 0.0 | 2.0 | 46 |
| NaMA | 0.0 | 5.3 | 31.5 |
| KMA | 0.0 | 6.0 | 36 |
| CsMA | 1.0 | 5.2 | 16.4 |
| CaMA | 0.2 | 3.0 | 39.5 |
| BaMA | 0.0 | 0.2 | 28.5 |
| SrMA | 0.1 | 6.5 | 27.5 |
| MgMA | 0.0 | 2.1 | 48.0 |
| ZnMA | 0.5 | 4.2 | 45.4 |

Table 3.8

TGA data: monomers degraded under N₂.



Carbon monoxide may form either instead of ketone as shown or by secondary reaction of metal carbonate and carbon. Carbon dioxide probably arises by the decomposition of metal carbonates as they are formed. In general, as the monomer salts seem to polymerize in the solid state on heating, a full account of the mechanism will be given in the next Chapter. Thermogravimetric analysis data is given in Table 3.8, in which weight losses at temperatures, 300, 400 and 500°C are summarised. It was found from the thermograms obtained, that monomer salts did not show any decomposition at temperatures below 300°C.

C H A P T E R F O U R

THERMAL DEGRADATION OF ALKALI METAL SALTS OF POLY (METHACRYLIC ACID)

The work described in this chapter forms part of a wider investigation of salts of polymethacrylic acid and the discussion will be limited to the degradation of alkali metal salts of the poly acid. Comparison will be made with the divalent metal salts in a subsequent chapter.

INTRODUCTION

Nothing has been published about the mechanism of decomposition of alkali metal salts of polymethacrylic acid. As described in chapter one, the mechanism of thermal degradation of polymers mostly depends on the polymer backbone and to some extent, on the nature of pendant groups. Therefore, before the results obtained from the thermal degradation of salts of methacrylic acid are discussed it would be feasible to make a brief comparison of polymethacrylate and polyacrylate esters and also some mention of degradation mechanism of salts of related aliphatic acids.

Although poly (methyl methacrylate) is the only poly (alkyl methacrylate) which degrades thermally to give quantitative monomer yield, all give monomer to some extent.

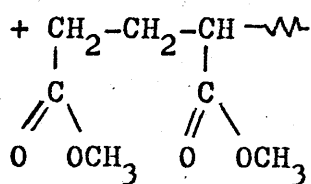
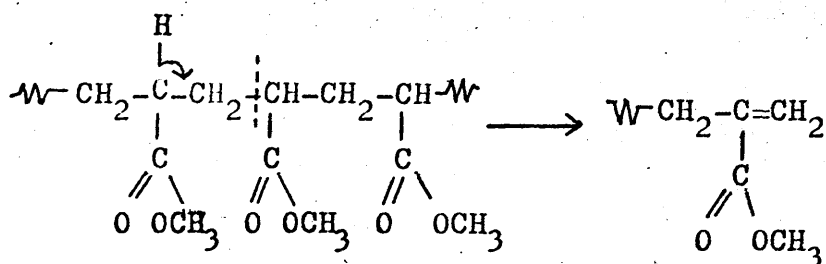
Grassie and Melville^{12,13,77} suggested that poly (methyl-methacrylate) depolymerises to monomer by free radical formation via random chain scission. The free radicals produced during the degradation are stabilized by resonance in the ester group. This stabilization gives enough time to form a double bond, and the monomer produced in this way is volatile at degradation temperature and distils out.

Thermal degradation of higher methacrylates has been studied by Grant and Grassie²⁵ for comparison of methyl, n-butyl, and t-butyl methacrylate polymers. Whereas poly (methyl methacrylate) has been shown to yield monomer as the overwhelming product of thermal decomposition, it was found that other esters did not exhibit similar behaviour. Grant and Grassie found that the most prominent volatile product from thermally degradation of poly (t-butyl methacrylate), was isobutene. The production of isobutene is clearly the result of an ester decomposition of simpler esters. The degradation of poly (t-butyl methacrylate) was carried out at 180°-200°C in vacuo, and the products were analysed individually at three different stages and interpreted in terms of three distinct reaction steps: (1) depolymerization in which monomer units are formed, (2) ester decomposition,

to yield isobutene and poly (methacrylic acid), and (3) anhydride formation in which the methacrylic acid units eliminate water. They also showed that monomer production has ceased almost entirely by the time significant amounts of isobutene are formed. Therefore depolymerization to monomer can occur in this system, but is inhibited by the products of ester decomposition. Grassie and MacCallum⁷⁸ reported that poly (ethyl methacrylate) and poly (n-butyl methacrylate) show a closely similar pattern of breakdown to that observed in the degradation of poly (t-butyl methacrylate). Therefore, one is forced to conclude from these studies that in poly (alkyl methacrylate) the structure of the alkyl portion (pendant group) of the chain (i.e. the presence or absence of β hydrogen atom) determines the course of the thermal degradation in at least the relative competition between the two reaction sequences.

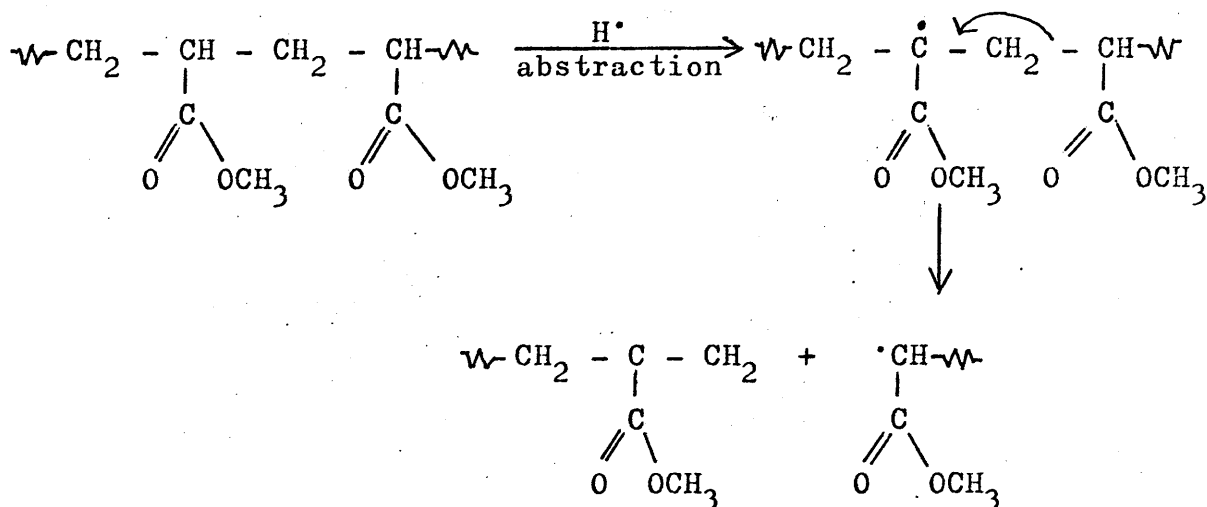
It is convenient at this stage to discuss the thermal breakdown of poly (methyl acrylate) briefly because the forthcoming discussion of the thermal degradation of poly (alkali metal methacrylates) will have some similarity with it.

Madorsky^{16,17} proposed that poly acrylates may not involve formation of free radicals during C-C bond scission in the chain and interpreted the data in the following manner:

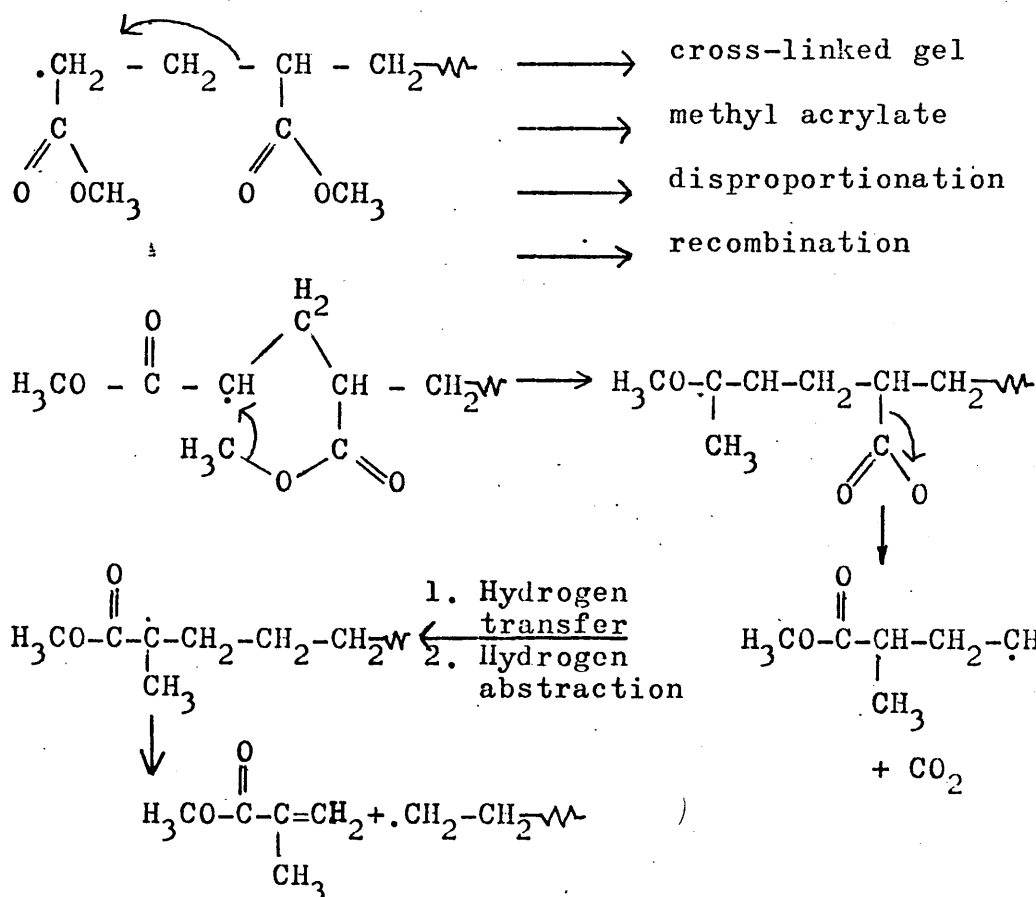


Cameron and Kane⁷⁹ have pointed out that the molecular weights of the fragments in the residue, on degradation of polymethylacrylate in the range of 286-300°C, are consistent with the random scission mechanism proposed by Madorsky;^{16,17} it was proposed that weak links might exist in the chain. They supported their proposal, showing that during the degradation the molecular weight of the residue fragments decreases rapidly. The data were obtained from viscosity measurements of the residue in benzene. Cameron and Kane⁷⁹ also found that the degraded polymer residues contained a portion of an insoluble gel. The presence of the gel is indicative of a cross-linking reaction in competition with the chain scission process. The proposed mechanistic scheme seems more logical as compared to the one proposed by Madorsky.^{16,17}

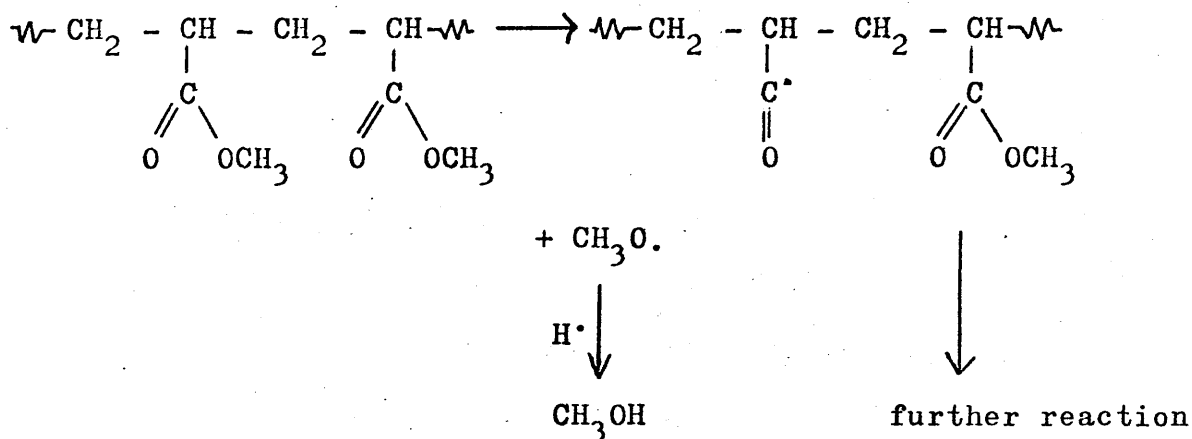
1. Initial degradation steps resulting in random chain scission.



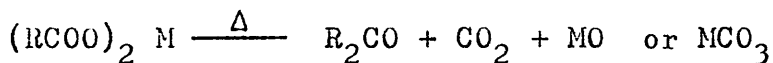
2. Reaction sequence proposed for the formation of crosslinked gel, carbon dioxide, methyl acrylate and methylmethacrylate.



3. Reaction proposed for the formation of methanol.



Decarboxylation of metal salts involves rearrangement, exemplified in the pyrolysis of metal carboxylates to give ketones, as:-

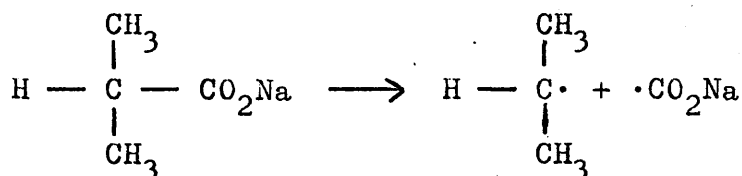


The dry distillation of calcium acetate to give acetone, is one of the oldest reactions in organic chemistry salts of other aliphatic acids also give ketones but the yields are frequently low and the products often difficult to purify.⁸⁰ There has been a great deal of work done on the mechanism of ketonic decarboxylation, but inspite of this only a relatively few definite conclusions can be reached.

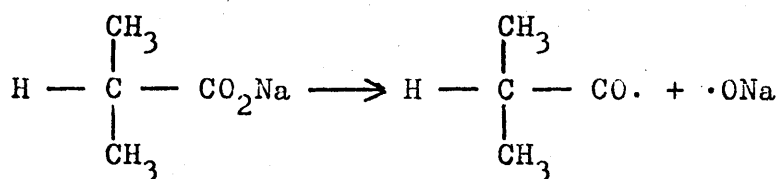
In the pyrolysis of calcium acetate Ardagh, Barbour, McClellan, and McBride⁸¹ reported that this reaction only became rapid at temperature 430°C although small traces of acetone were formed at temperatures as low as 160°C. The

high temperatures required for rapid reaction are consistent with the formation of free radicals and it is suggested that the high temperature reaction proceeds by a chain mechanism, initiated either by the formation of free methyl radicals, or by free formyl radicals. It is considered that the reaction is initiated by the free methyl radical, a view favoured by the following observations.

Cook, Miller, and Whitmore⁸² have reported the formation of a small quantity of n-propyl isopropyl ketone in addition to the expected diisopropyl ketone, formed by passing isobutyric acid vapour over heated thorium. O'Neill and Reed⁸³ have shown that pyrolysis of sodium isobutyrate, a compound which decomposes about 400°C, yields a substantial quantity of di n-propyl ketone and n-propyl isopropyl ketone as well as the expected diisopropyl ketone. These results can most readily be interpreted by assuming that rearrangement occurred in an intermediate radical and it is considered that this evidence favours the process:

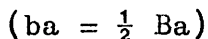
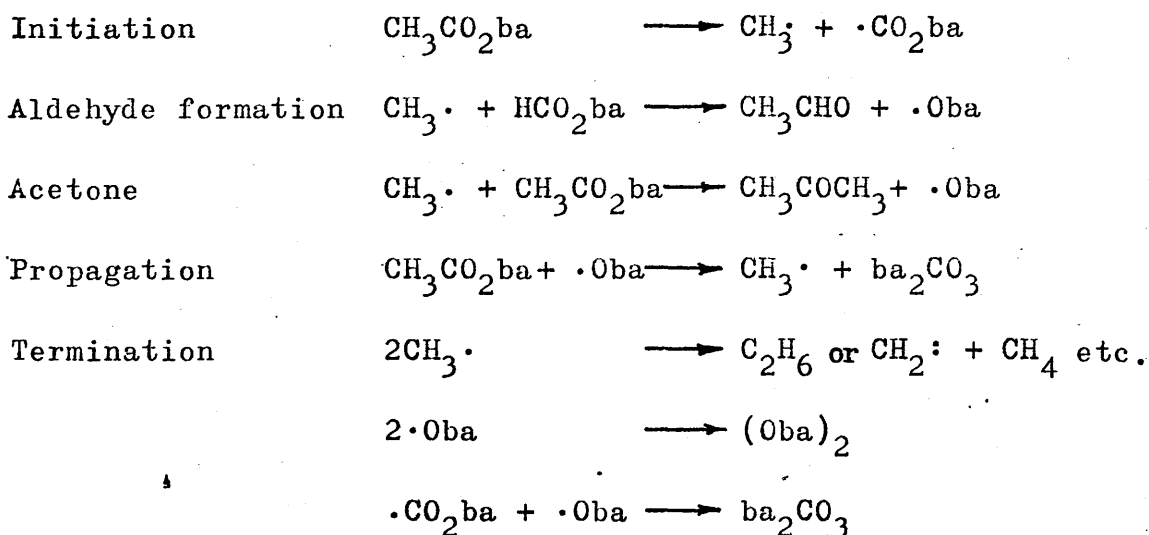


followed by rearrangement of the alkyl radical, rather than:



in which the alkyl group which undergoes rearrangement does not contain the electron-deficient centre.

The above chain mechanism is also in general agreement with the one proposed by Bell and Reed,⁸⁴ who studied the pyrolysis of barium acetate and formate mixtures, using isotopic tracer techniques, and produced the following reaction scheme to explain the formation of acetone and acetaldehyde:-



In the decomposition of acid salts, the relative importance of the metal is obscure, and there is no evidence to decide whether the salt reacts in the covalent form as indicated in the above reaction scheme, or whether the reaction occurs between the carboxylate ions. The former postulate is preferred as considerable evidence has been accumulated in the literature,^{85,86} which shows that the yield

of acetone varies markedly with variation of the metal even when such changes are restricted to alkali and alkaline-earth metals.

Although the above mentioned schemes are not strictly applicable to the acetate or isobutyrate system alone, it does serve to illustrate some of the many possible reaction pathways which can occur during decomposition of the metal salts of acids.

EXPERIMENTAL

Details of preparation and history of the homopolymers are given in chapter two.

RESULTS AND DISCUSSION

As the homopolymers absorb moisture from the atmosphere it was necessary to determine the amount of moisture absorbed. This was done by thermogravimetry. All the sample sizes described in the forthcoming discussion refer to the pure homopolymers excluding moisture and precipitant.

THERMAL VOLATILIZATION ANALYSIS

The homopolymers were examined in powder form and the sample sizes were 50-60 mg, degraded up to 500°C and the heating rate 10°/min under the normal TVA conditions.

TVA traces for lithium, sodium, potassium and caesium poly methacrylate are shown in Figs. 4.1, 4.2, 4.3 and 4.4 respectively. All four traces are very similar, with T_{\max} values of about 450°C. For LiPMA and NaPMA, the 0° and -45°C traces are co-incident, indicating absence of condensation at

-45°C, but the -75° and -100° curves are well apart from those of 0° and -45°, showing that the expected ketones are condensing in these traps. The lack of coincidence of the -75°, -100° and -196°C traces also suggests that there are several other products, some of which are non-condensable at -196°C. The separation between 0°, -45°, -75° and -100°C decreases as the size of the metal ion increases, which suggests that the amount of ketones or high boiling volatiles decreases as the size of the metal ion increases. The coincidence of all five traces in the case of KPMA and CsPMA may be because of larger amounts of non-condensables produced as compared to LiPMA and NaPMA.

It is clear from the TVA traces that volatile material including a non-condensable fraction appears at a temperature around 330°C (T_{base}) and the maximum rate of volatilization occurs around temperature 450°C (T_{max}). T_{max} 's and T_{base} s for the homopolymer TVA traces are summarised in Table 4.1.

| Homopolymer. | $T_{\text{base}} \text{ } ^\circ\text{C}$ | $T_{\text{max}} \text{ } ^\circ\text{C}$ |
|--------------|---|--|
| LiPMA | 352 | 444 |
| NaPMA | 344 | 454 |
| KPMA | 340 | 447 |
| CsPMA | 332 | 447 |

Table 4.1

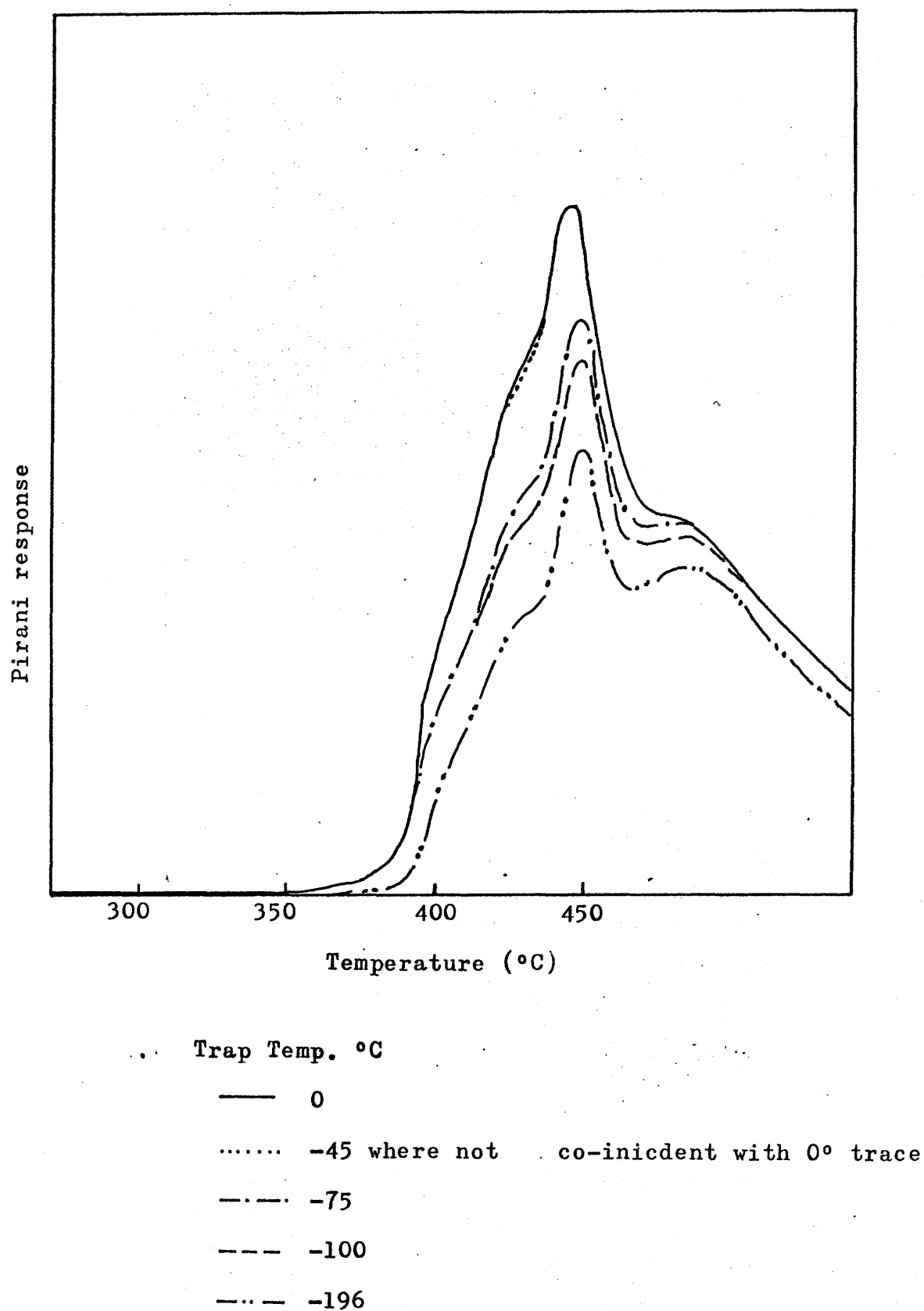
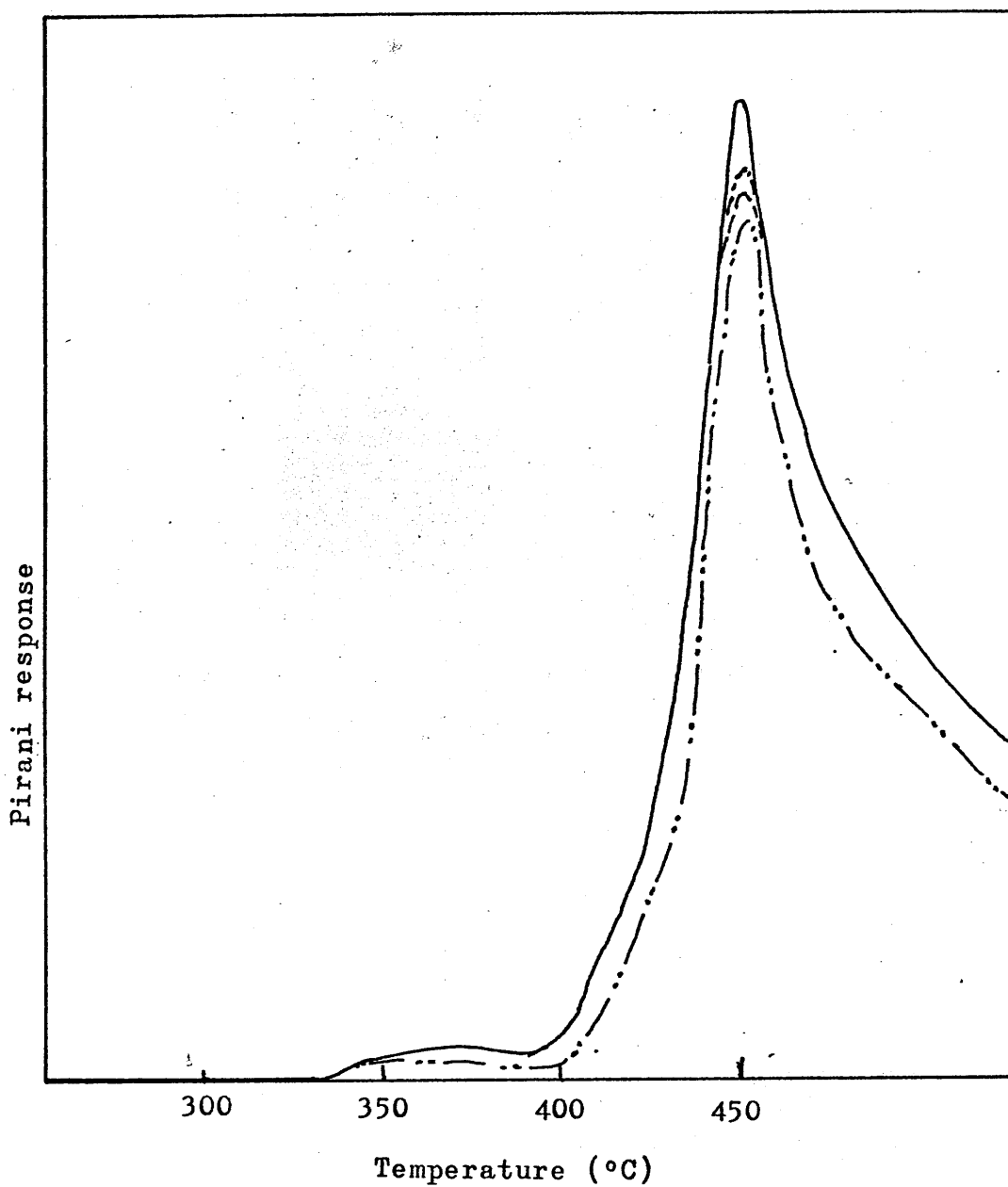


Fig. 4.1 TVA curve for lithium polymethacrylate



Trap Temp. °C

— 0 and -45

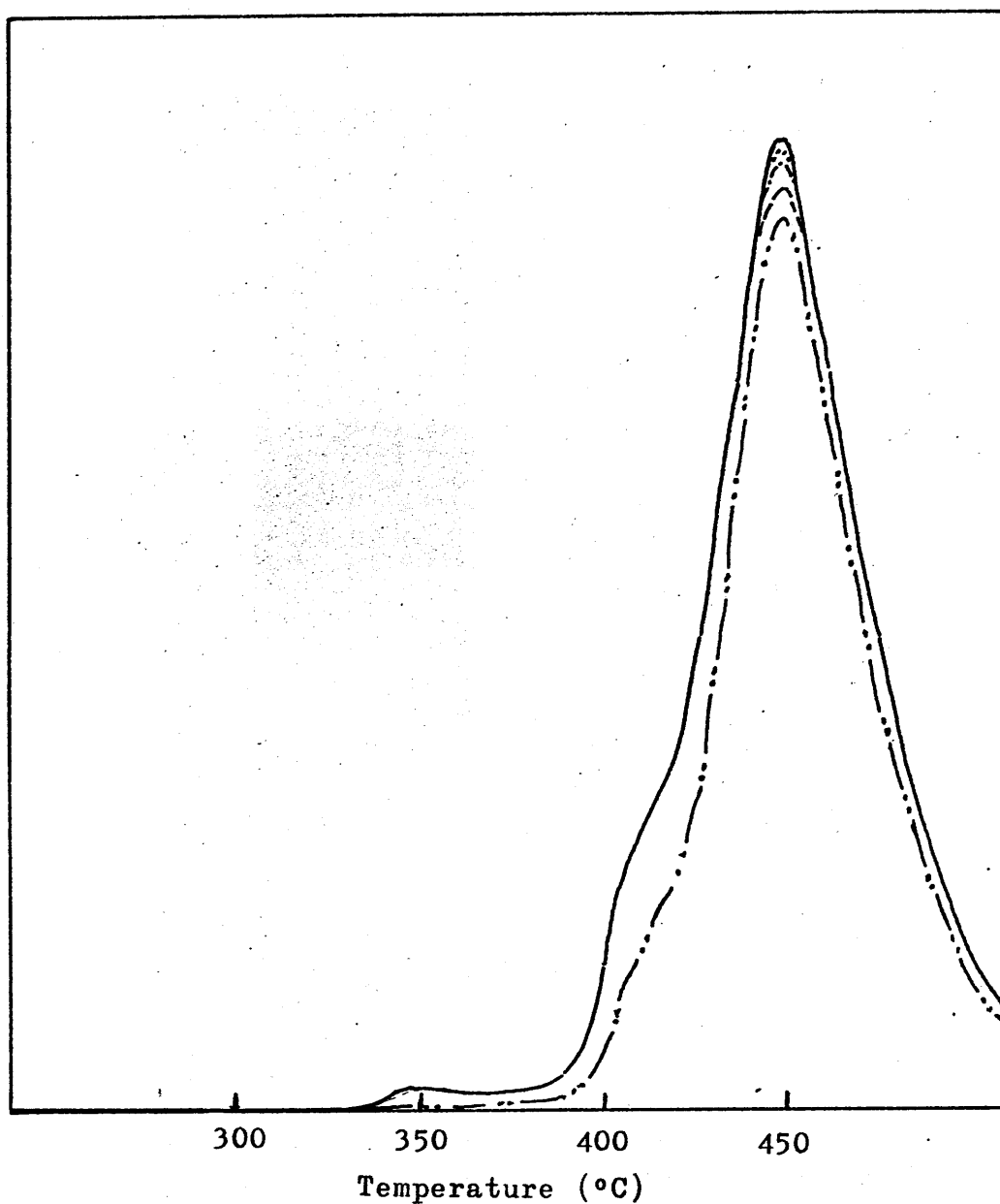
..... -75 where not co-incident with 0 and -45° traces

--- -100 where not co-incident with 0, -45 and -75° traces

- · - · - -196

Fig. 4.2 TVA curve for sodium polymethacrylate

Pirani response



Trap Temp. °C

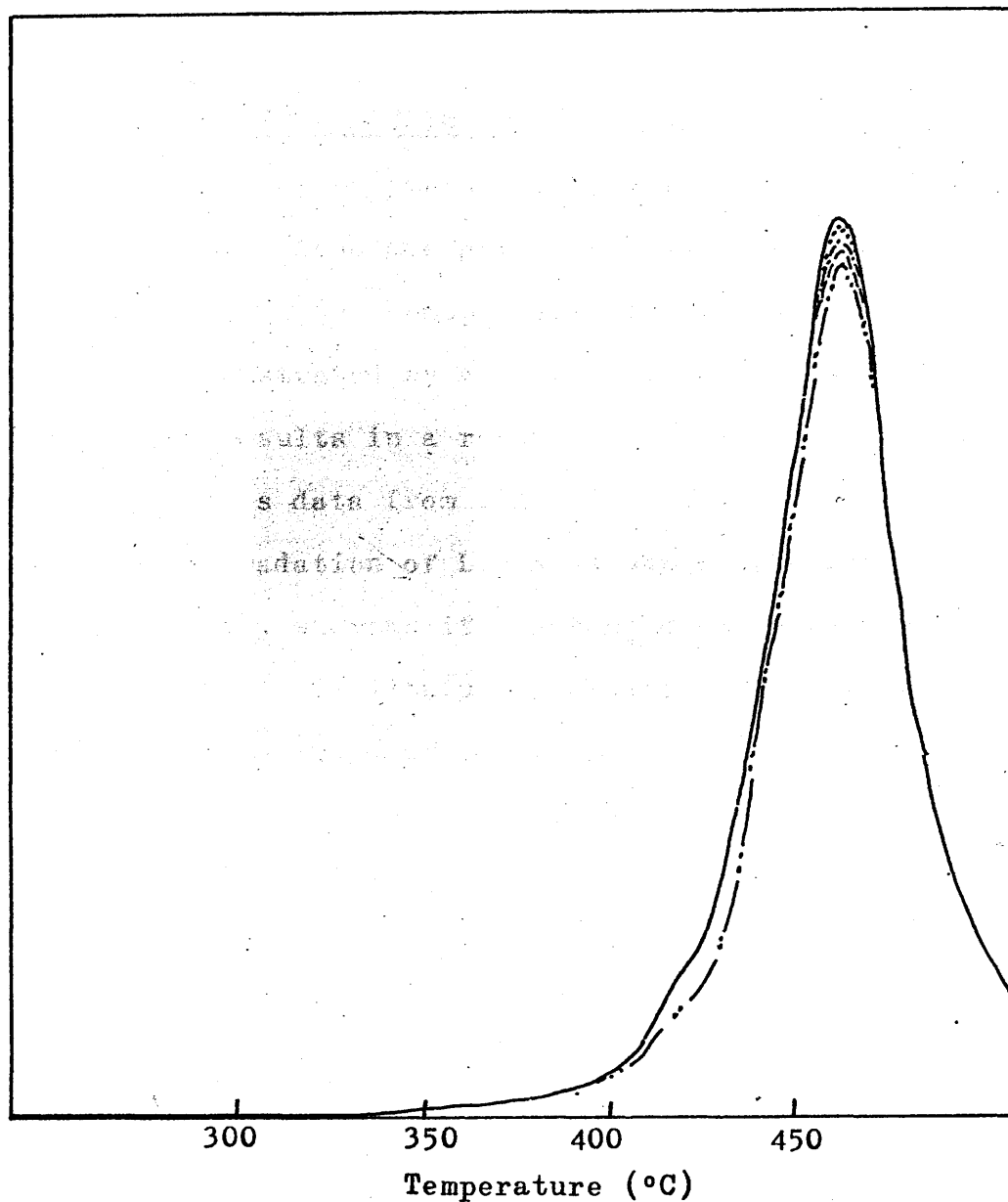
— 0

..... -45 where not co-incident with 0° trace

-.-.- -75 where not co-incident with 0 and
-45° traces--- -100 where not co-incident with 0,
-45 and -75° traces

-.-.- -196

Fig. 4.3 TVA curve for potassium polymethacrylate



Trap Temp. °C

— 0

..... -45 where not co-incident with 0° trace

-.- -75 where not co-incident with 0 and
-45° traces

--- -100 where co-incident with 0,
-45 and -75° traces

-...- -196

Fig. 4.4 TVA curve for caesium polymethacrylate

THERMOGRAVIMETRIC ANALYSIS

TGA curves of polymers degraded under oxygen-free nitrogen and in vacuo are given in Figures 4.5, 4.6, 4.7 and 4.8. For all the homopolymers a one-stage degradation is clearly illustrated by a pronounced one-stage weight loss curve, which results in a residue at 500°C.

Weight loss data from TGA gave the fraction of residue left after degradation of LiPMA as 54% of the weight of the original sample, whereas if the sample was pure homopolymer degraded entirely to lithium carbonate, the residue should account for only 42.2% of the weight of the original sample, suggesting the presence in the residue of some other relatively inert species, possibly carbon.

Weight loss data for NaPMA, KPMA and CsPMA gave the residues to be 63.5%, 66% and 82% of the weight of the original polymer (solvent corrected) as opposed to 49.05%, 55.66% and 74.77% which would be expected if degradation was entirely to the respective carbonates. The percentage of residue from the original sample if degraded under nitrogen is different from that of the percentage of residue left, if the same sample is degraded under vacuum. This anomaly appears in all these homopolymers, as the TGA curves show in the respective figures. One example is the case of NaPMA, which leaves a residue, 63.5%, if degraded under nitrogen, but 49% residue under vacuum. This marked difference is attributed to the short chain fragments (including some monomer) which escape from the hot zone to the cold ring of

the TVA tube under high vacuum conditions, while these fragments fail to do so under nitrogen pressure. IR spectroscopic investigation of short chain fragments shows the presence of carboxylate ions, which are less likely to volatilise or sublime under ordinary conditions, hence marking the difference in degradation under different conditions. The thermal break down of the homopolymer starts at approximately the same temperature under vacuum and in nitrogen.

The % of weight losses under different conditions are listed in Table 4.2.

| Homopolymer | Percentage of weight loss | |
|-------------|---------------------------|--------------------|
| | under N ₂ | under vacuum (TVA) |
| LiPMA | 46.0 | 50.0 |
| NaPMA | 36.5 | 49.0 |
| KPMA | 34.0 | 51.0 |
| CsPMA | 18.0 | 49.0 |

weight losses at 500°C Table 4.2

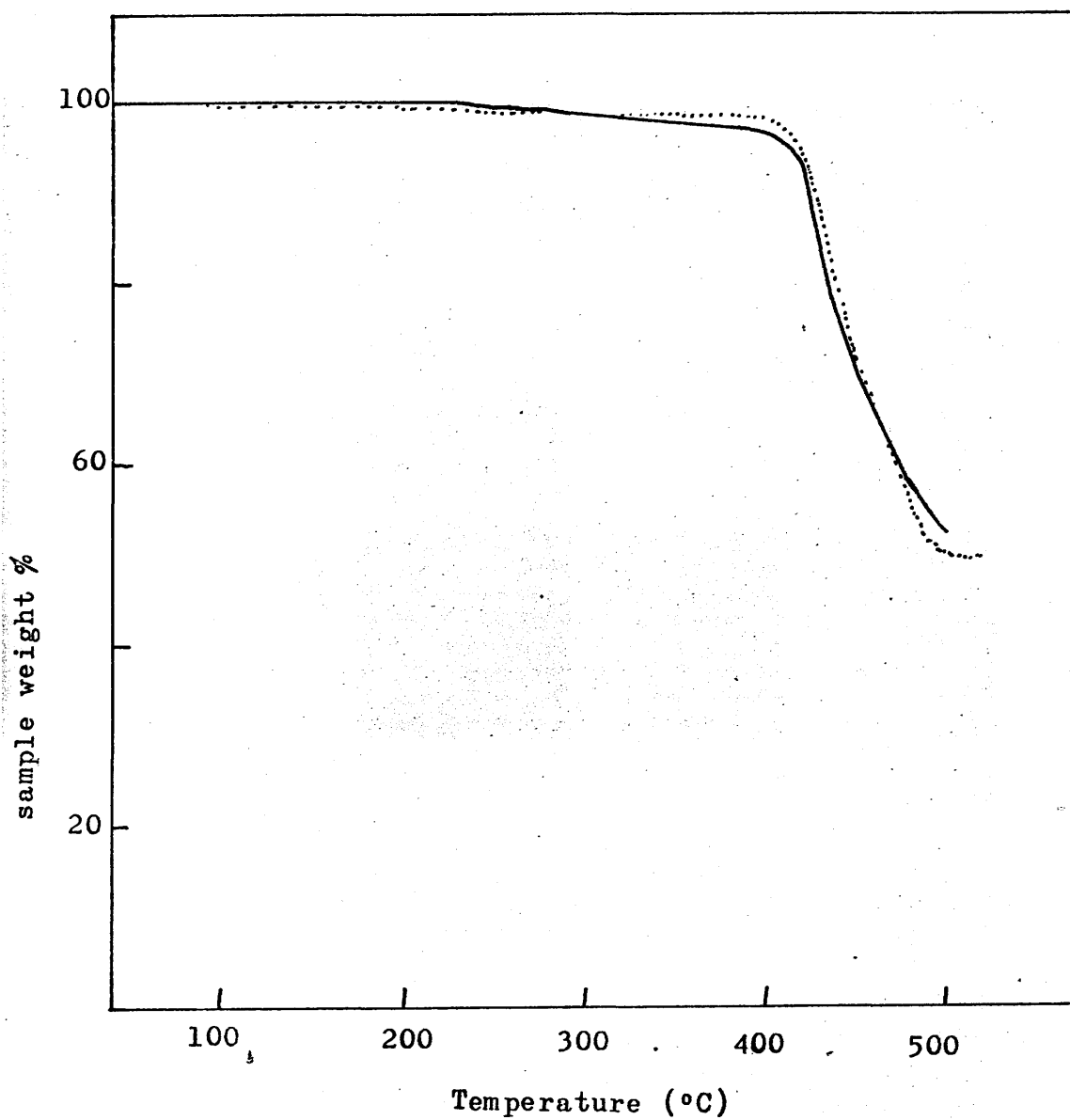


Fig. 4.5 TG curves for lithium polymethacrylate,
heating rate 10°C/min

— dynamic N₂ atmosphere

..... vacuum

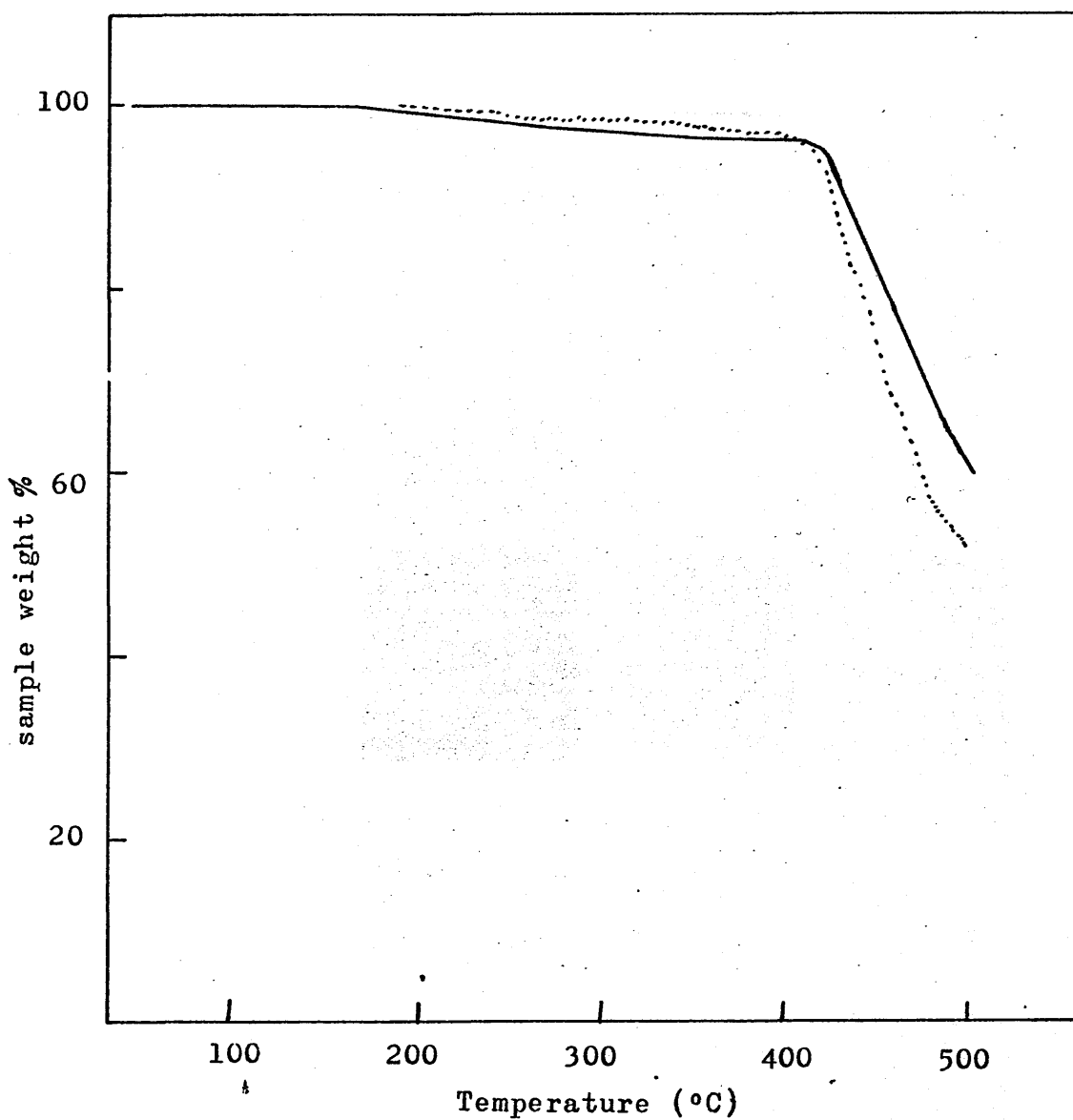


Fig. 4.6 TG curves for sodium polymethacrylate,
heating rate 10°C/min

— dynamic N₂ atmosphere
..... vacuum

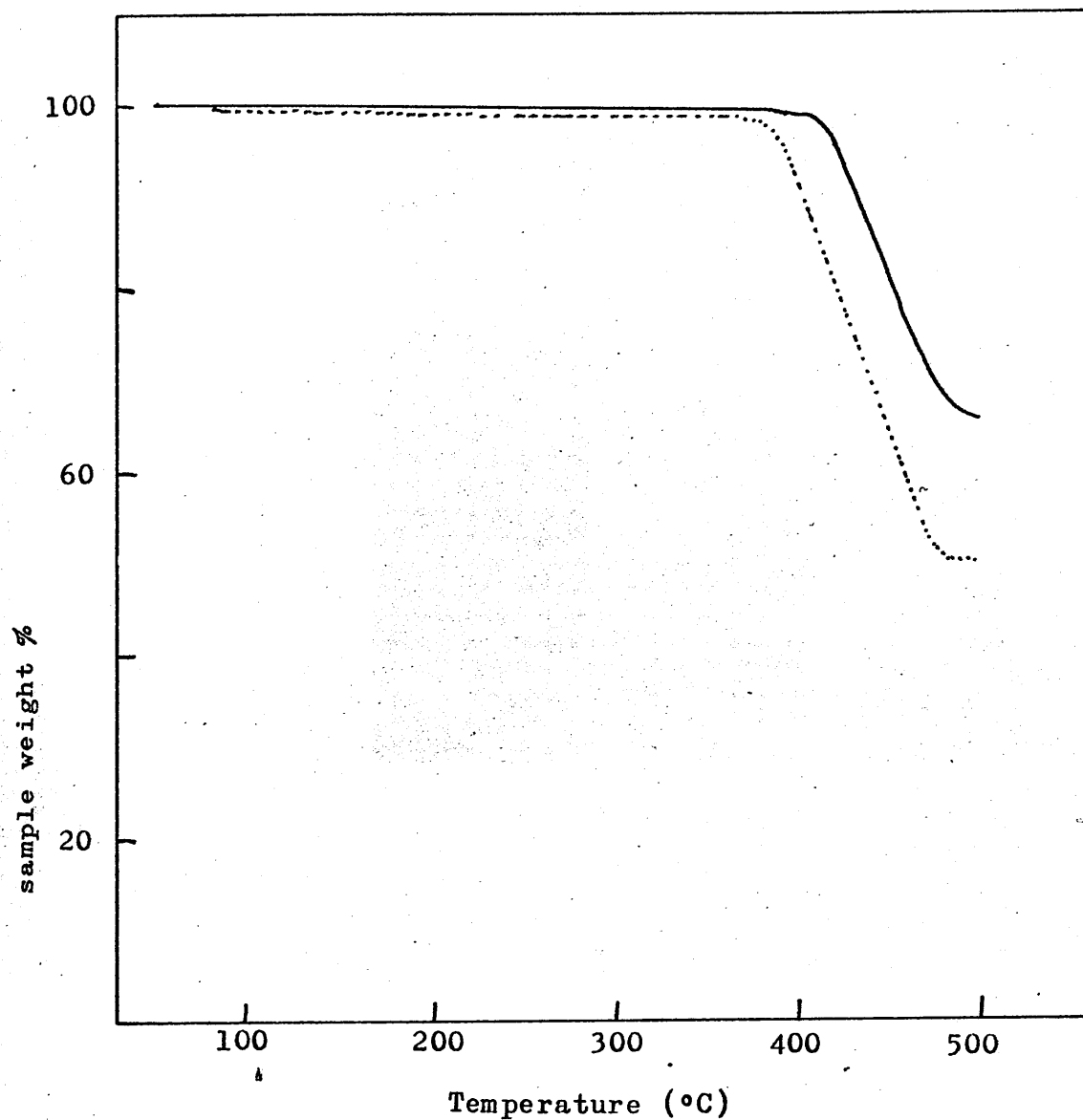


Fig. 4.7 TG curves for potassium polymethacrylate,
heating rate 10°C/min

— dynamic N₂ atmosphere
..... vacuum

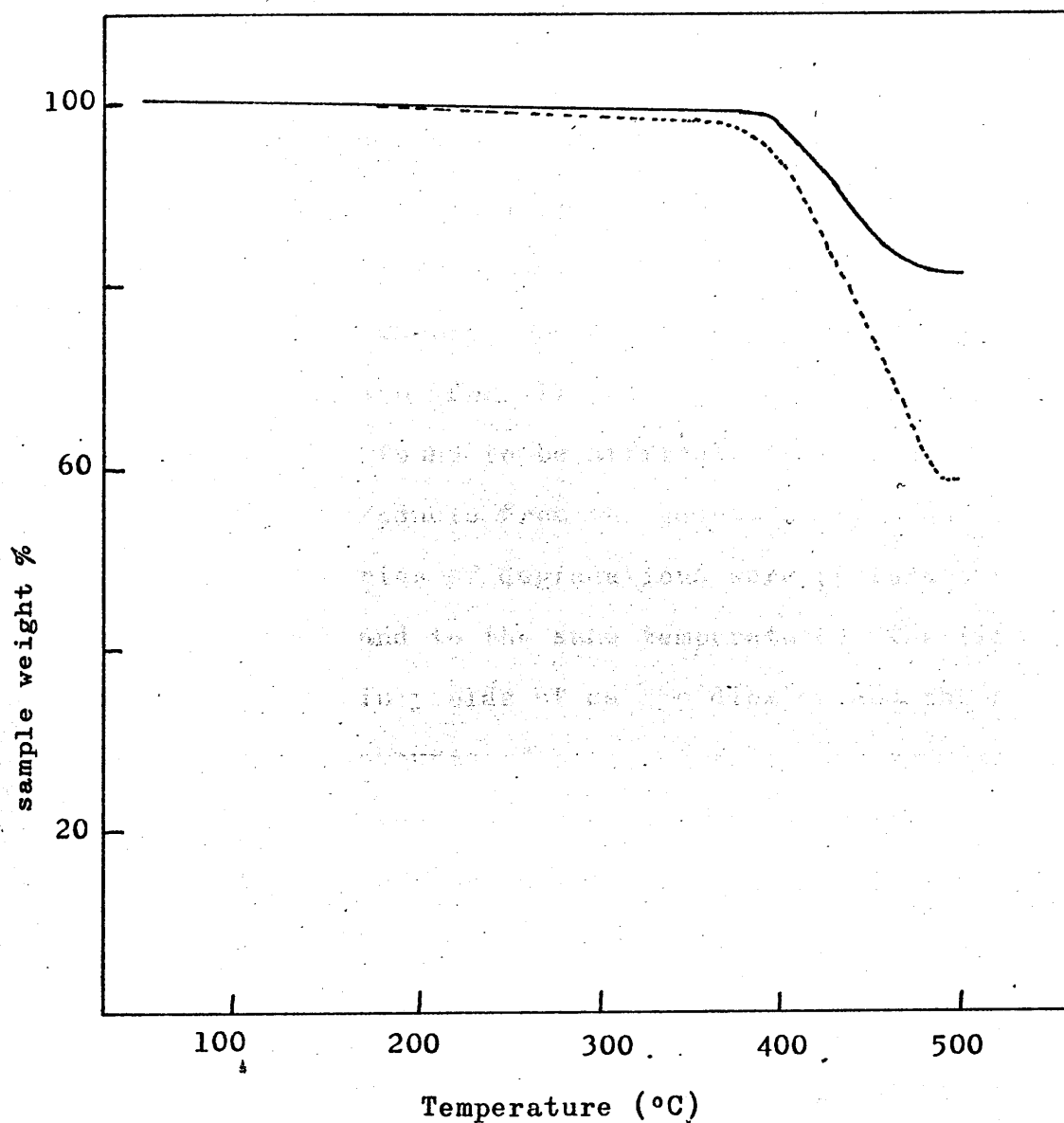


Fig. 4.8 TG curves for caesium polymethacrylate,
heating rate 10°C/min.

———— Dynamic N₂ atmosphere
 vacuum

ANALYSIS OF VOLATILES

Analysis of the volatiles was carried out by using the techniques mentioned in Chapter 2.

Although in theory, one set of degradation experiments should be sufficient for all the significant products to be analysed, it was found to be difficult to separate the low boiling liquid products from the gases, olefins and carbon dioxide. Two series of degradations were performed under the same conditions and to the same temperature. The first series was used to obtain yields of carbon dioxide and the second series gave the amounts of other degradation products. Where only qualitative results were required, data were obtained from either degradation series.

IR ANALYSIS OF VOLATILES

IR spectra were obtained of the gaseous degradation products from the four homopolymers. The sample sizes were 100 mgs. to 150 mgs., and degradations were carried out at 10°C/min. from room temperature to 500°C under normal TVA conditions, except for analysis of products non-condensable at -196°C, when a closed system was used. In order that residual precipitant and absorbed moisture from the sample would not be included, the cold traps were raised, only when all the precipitant and absorbed moisture had escaped from the sample. Due to the overlap of the C=O stretching frequencies of the variety of ketones and aldehydes, it was not possible to assign the peaks to individual carbonyl

containing volatiles, which instead were identified by gas chromatography. The peaks assigned to the other gaseous volatiles were identified by the use of reference spectra.

The IR spectra of the volatiles from the four homopolymers, are almost identical differing only in amounts of volatiles.

A typical spectrum of the degradation products from KPMA is shown in Fig. 4.9 and the assignments of the peaks are summarised in Table 4.3.

Table 4.3

Assignment of IR peaks of degradation products of KPMA

| Frequency cm ⁻¹ | Mode | Compound or group |
|-------------------------------|--|--|
| 3018 | C-H stretching | Methane |
| 2845-2965 | C-H " | CH ₃ , CH ₂ , CH |
| 2340 | C-O " | Carbon dioxide |
| 2145 | C-O " (fine spectrum) | Carbon monoxide |
| 1740 (Broad) | C=O " | Carbonyl |
| 1640-1665 | C=C " | - |
| 1445-1465 | →C-H deformation | - |
| 1325 (Broad) | -CH ₃ symmetrical deformation | -CH ₃ |
| 1308 | -CH ₃ " " | Methane |
| 1215 br-1170 | C - C - C skeletal O | Ketones |
| 990 | C-H out of plane deformation | -CH=CH- trans |
| 950 | C-H " " " " | Ethylene |
| 912 | C-H " " " " | Butene-1 |
| 900 | C-H " " " " | |
| 890 | C-H " " " " | Isobutene |
| 732 | C-H " " " " | Acetylene |
| 721 | C-O bend | Carbon dioxide |
| 690 | C-H " | Toluene |
| 675 | C-H " | Benzene |
| 669 | C-O " | Carbon dioxide |

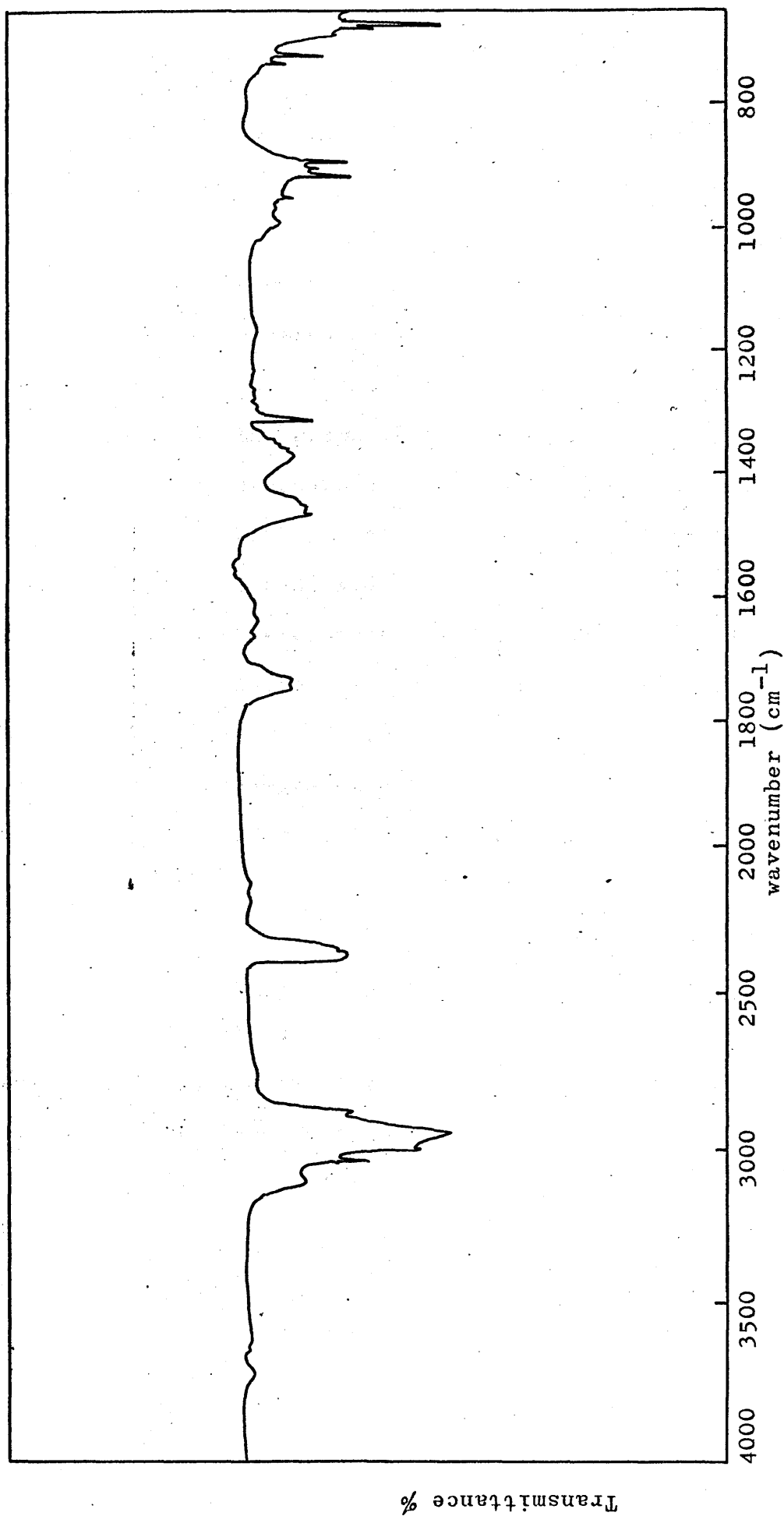


Fig. 4.9 IR spectrum of gaseous volatiles evolved by decomposition to 500°C of potassium polymethacrylate.

QUANTITATIVE IR ANALYSIS OF CARBON DIOXIDE

Quantitative analysis of the total carbon dioxide produced from the homopolymers was carried out by infra-red spectroscopy as described in Chapter 2. The mole percentage gas evolved (based on weight of pure polymer) by each of the homopolymers was plotted against the ionic radius of the corresponding cation of the homopolymer as shown in Fig. 4.10. It is clear from the graph that a gradual enhancement of carbon dioxide production occurs as the ionic radius increases ($\text{Li}^+ \text{ --- } \text{Cs}^+$). This linear relationship between the production of carbon dioxide and the size of the metal ion suggests that the percentage of metal oxide formation during the degradation, increases and the opposite is true for carbonate formation. The formation of metal oxide can occur either during the degradation of the polymer or it may be formed by secondary reaction, such as the decomposition of the metal carbonate.

Lithium carbonate⁶⁷ is relatively thermally unstable with respect to lithium oxide and carbon dioxide compared to the other alkali metal carbonates, because the small lithium ion makes the lithium oxide lattice more stable than are the other metal oxide lattices as compared to the metal carbonates lattices. Thermodynamically ΔH_0 for alkali metal oxide⁸⁷ formation increases from Li^+ to Cs^+ . These ΔH_0 values were calculated at 450°C (the T_{max} 's of TVA thermogram) by applying the following method.⁸⁷

$$\Delta G = \Delta H_0 + 2.303 a T \log T + b \times 10^{-3} T^2 + C \times 10^5 T^{-1} + IT$$

$$\Delta S = -a - 2.303 a \log T - 2b \times 10^{-3} T + C \times 10^5 \times T^{-2} - I$$

The values of a , b , C and I are tabulated elsewhere⁸⁷ and by substituting these, ΔG and ΔS can be calculated at certain temperatures and then by applying the following equation ΔH can be calculated.

$$\Delta G = \Delta H - T\Delta S$$

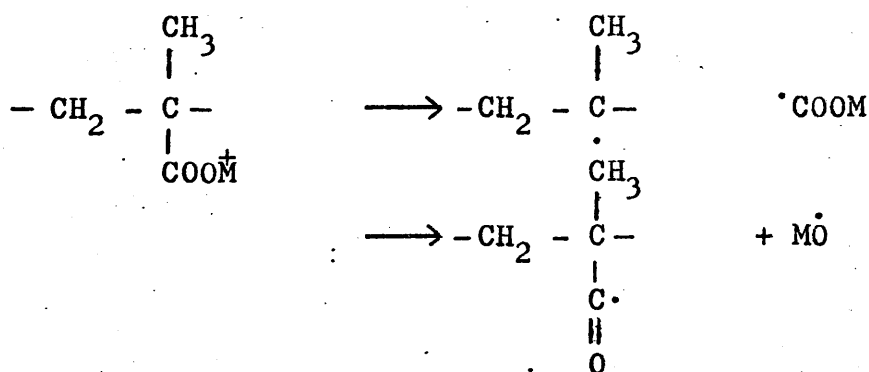
ΔH values at temperatures 298°K and 723°K are given in Table 4.4. The ΔH_{298} were plotted against the ionic radii, shown in Fig. 4.11. It is obvious from the graph that ΔH_{298} of Li_2O is very low as compared to that of Cs_2O , suggesting that the formation of lithium oxide would be more favourable as compared to caesium oxide. The lattice energies consideration and ΔH_{298} data are not in agreement with the practical data obtained for carbon dioxide from the homopolymers.

The above anomaly seems to have arisen from the decomposition of metal carbonate formed during the degradation of the polymers. To demonstrate this, all four metal carbonates were degraded under normal TVA conditions up to 500°C at the rate of 10°C/min and carbon dioxide was measured quantitatively. It was found that potassium and caesium carbonate decomposed while lithium and sodium carbonate remained stable.

ΔH_{298} values for the reaction $M + C + \text{O}_2 \longrightarrow \text{M}_2\text{CO}_3$ are listed in Table 4.4 and if these are plotted against the ionic radii (Fig. 4.12), a straight line is obtained with sodium just out. This data shows that ΔH of lithium carbonate is more

negative compared to that of caesium carbonate, therefore the formation of lithium carbonate would be more favourable compared to caesium carbonate. It has been shown in the earlier part of this discussion that lithium carbonate and sodium carbonate do not decompose at temperature 500°C under vacuum and this makes the production of carbon dioxide from LiPMA and NaPMA, ambiguous.

In view of the above discussion it seems that formation of metal oxide and carbonate may not involve ionic processes, but these may form via free radical mechanisms.



This type of mechanism would be more favourable in the case of a polymer chain containing syndiotactic segments because of a large number of unreactive monomer units in the chain during degradation. It has been stated in Chapter I that syndiotacticity

| $2M + \frac{1}{2}O_2 \longrightarrow M_2O$ | | | $4M + 2C + 3O_2 \longrightarrow 2M_2CO_3$ | |
|--|------------------------------------|-------------------------------------|---|-------------------------------------|
| Metal Oxide | $\Delta H_{298^\circ K}$ | $\Delta H_{723^\circ K}$ | Metal Carbonate | $\Delta H_{298^\circ K}$ |
| Li ₂ O | -142.4 K cal mole ⁻¹ | -141.48 K cal mole ⁻¹ | Li ₂ CO ₃ | -290.54 K cal mole ⁻¹ |
| Na ₂ O | -100.15 " | *-115.58 " | Na ₂ CO ₃ | -270.3 " |
| K ₂ O | -87.38 " | -87.74 " | K ₂ CO ₃ | -273.93 " |
| Cs ₂ O | -75.9 " | -75.9 " | Cs ₂ CO ₃ | -267.4 " |

Table 4.4

ΔH values of metal oxide and metal carbonate

* This value is evidently anomalous.

of these polymers increases as the size of the metal ion increases, therefore production of carbon dioxide and formation of metal oxide will increase with the size of metal ion.

Apart from the above explanations given, further investigations are needed by X-ray diffraction and electron microscopy in order to observe the possibility of formation of metal suboxide, peroxide and superoxide, during the course of degradation of homopolymers. The chances for the formation of peroxide and superoxide, though, seem to be very remote under high vacuum conditions as a high pressure of oxygen atmosphere is required to convert the oxides to superoxides, but they may form via a free radical mechanism.

| Homopolymer | Mole % of CO ₂ | Metal Carbonate | Mole % of CO ₂ |
|-------------|------------------------------|--|------------------------------|
| LiPMA | 5.4 | Li ₂ CO ₃ | - |
| NaPMA | 15.9 | Na ₂ CO ₃ | - |
| KPMA | 21.8 | K ₂ CO ₃ | 2.5 |
| CsPMA | 31.3 | Cs ₂ CO ₃ ·2H ₂ O | 30.4 |

Table 4.5

Mole % of CO₂ produced from homopolymer and metal-carbonates

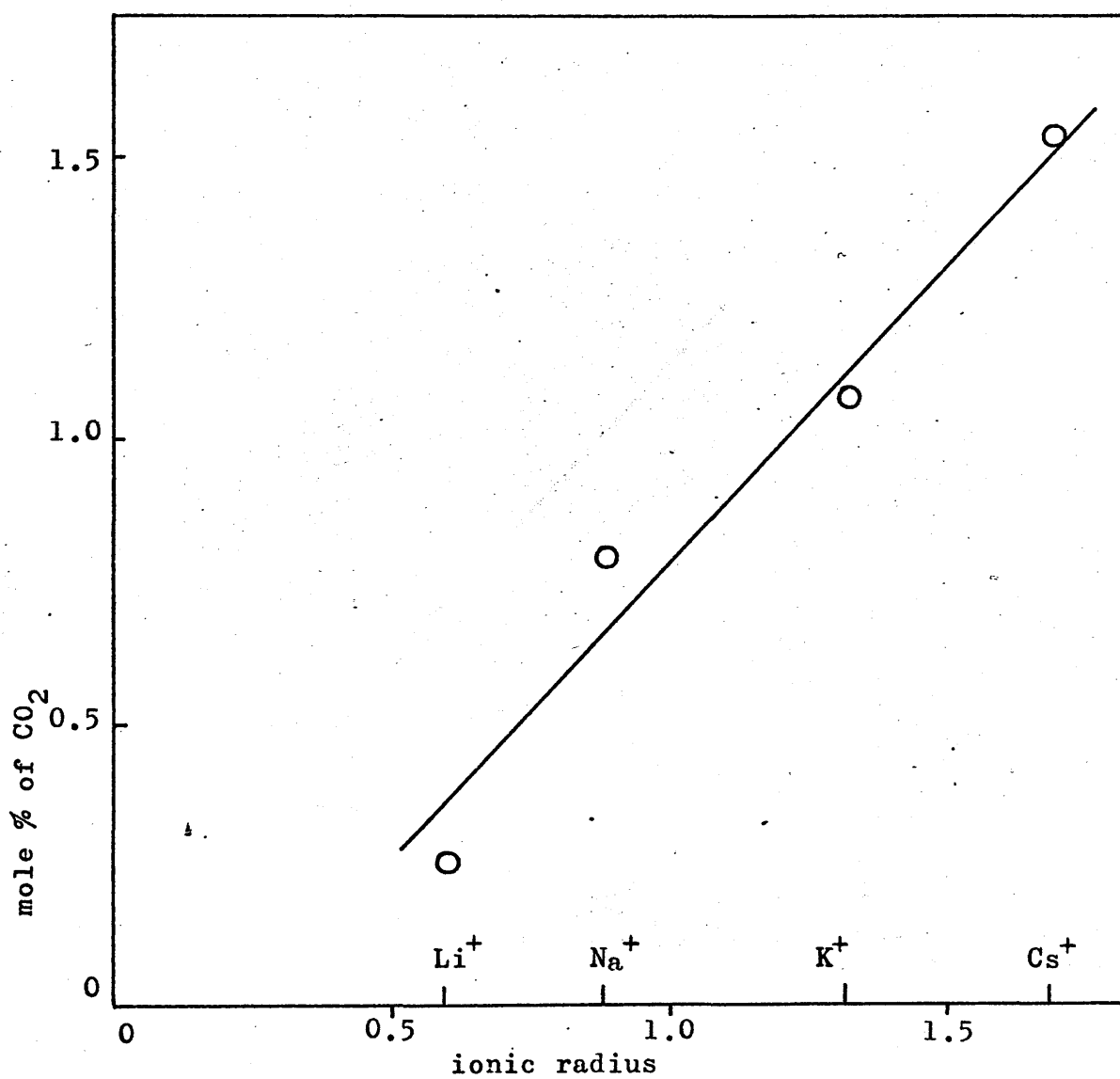


Fig. 4.10 Evolution of carbon dioxide versus ionic radius of the corresponding cation of the homopolymer.

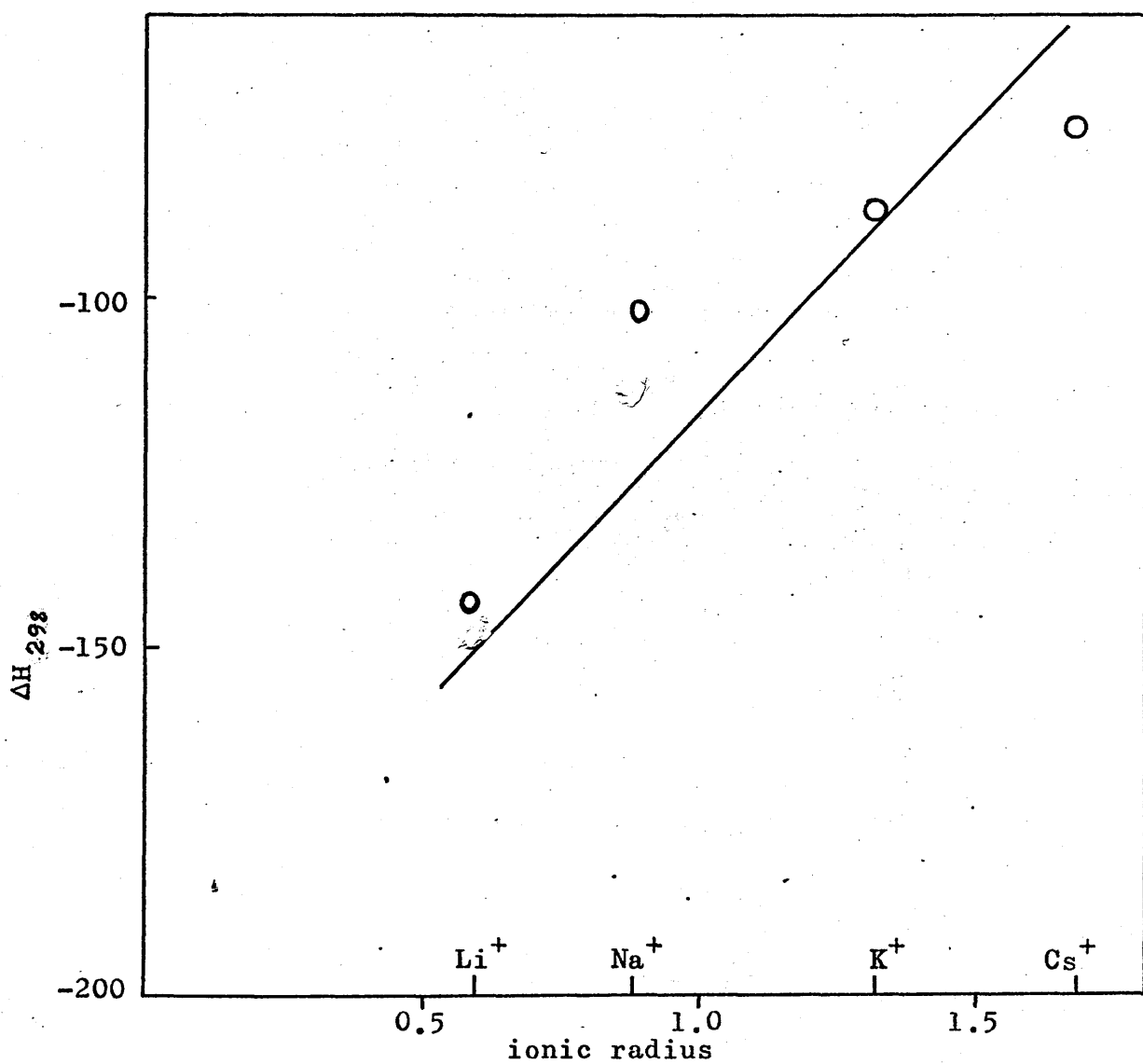


Fig. 4.11 $\Delta H_{\text{hyd}} (2\text{M} + \text{O}_2 \rightarrow 2\text{M}_2\text{O})$ versus ionic radius

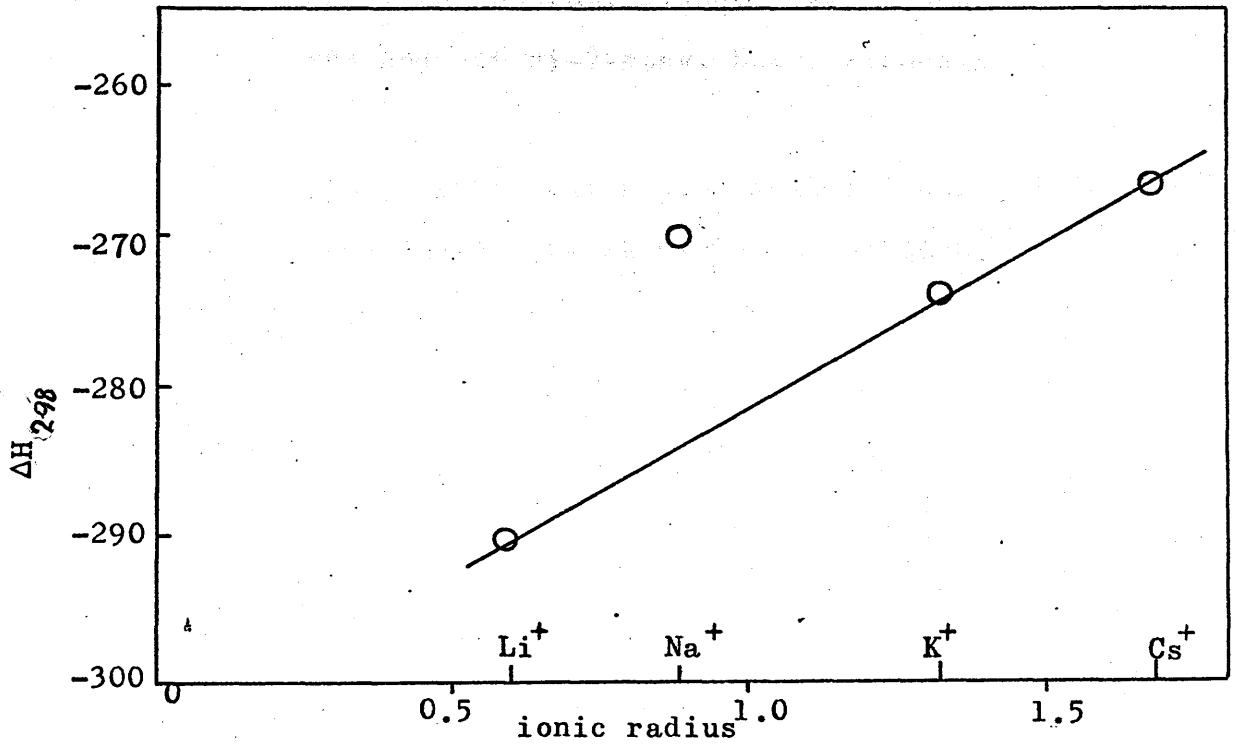


Fig. 4.12 $\Delta H_{298}^{\circ}(4M+3O_2+2C \rightarrow 2M_2CO_3)$ versus ionic radius.

LIQUID PRODUCTS ANALYSIS BY GAS-LIQUID CHROMATOGRAPHY (GLC)

GLC was performed on liquid volatiles (without fractionation) from TVA degradation at 10°C/min to 500°C of a 100-150 mg powder sample of each polymer, the products collected, weighed and analysed as described in Chapter 2, using n-butyl alcohol as internal standard and a column containing 13½% MEA and 6½% di-2-ethyl hexyl sebacate on chromosorb.

Aldehydes, methyl ethyl ketone and methyl isopropyl ketone were separated using the above column at 50°C; diethyl ketone, methyl n-propenyl ketone and methyl isopropenyl ketone at 60°C and cyclic ketones were determined at 70°C isothermally.

Altogether, there are twenty-six peaks, peak A is of air, B of ether (retained by the syringe after cleaning), C of methanol (the polymer precipitant) and peak D is of chloroform (retained by the degradation apparatus during cleaning), and therefore these peaks are not accounted as degradation products. The rest of the peaks were determined by injecting reference compounds and then by comparing their retention times with the unknown traces of the degradation products. Only a little shoulder designated as peak (10) and a minor trace of peak (13) are unidentified. The mole percentage yields of the volatiles evolved by each of the homopolymers are listed in Table 4.6 and the traces obtained from LiPMA degradation are shown in Fig. 4.13. The number of liquid volatiles determined from all the homopolymers was found

to be the same, but differing in their relative amounts, particularly in the case of cyclic ketones, which show a relationship between their production from the degradation of the homopolymers and the ionic radii of the metals in the polymers. The graph in Fig. 4.14 shows a gradual increase of mole % yield of the total cyclic ketones as the size of ionic radius ($\text{Cs} \rightarrow \text{Li}$) decreases, which is again the result of syndiotacticity of the polymer. Only intramolecular elimination of metal carbonate can result in the formation of cyclic ketones, as they are all composed of at least five carbons. The effect of the tacticity of the homopolymers can be more clearly examined from the graph (Fig. 4.15). The mole % yield of dimethyl cyclopentenone decreases as the size of ion increases and its formation is the straight forward result of intramolecular elimination of metal carbonate, rather than intermolecular, which will crosslink the chains.

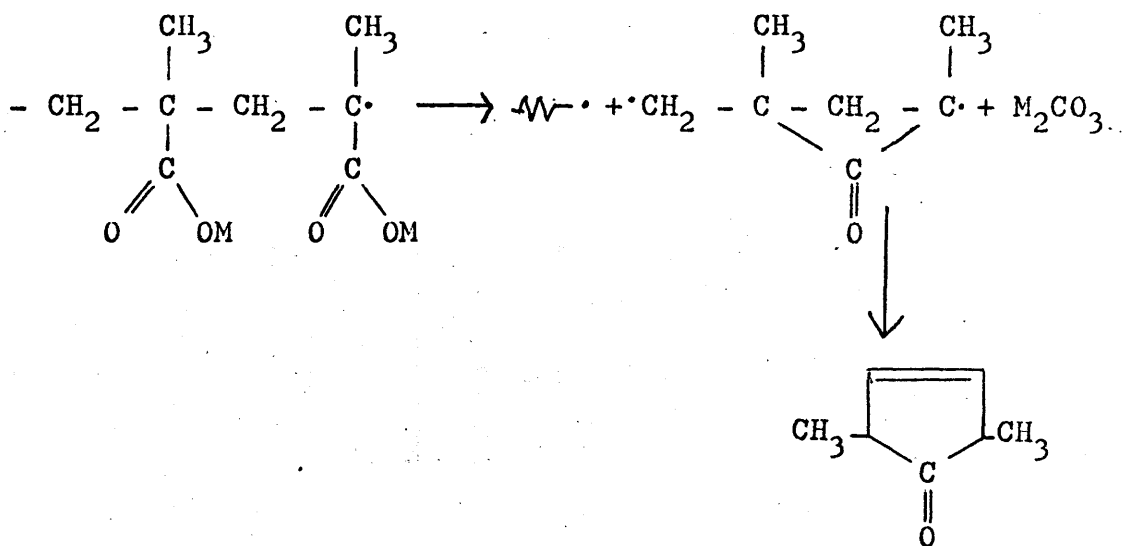


Table 4.6

Mole % Yield of Liquid Volatiles from the Homopolymers

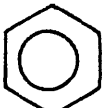
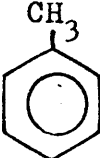
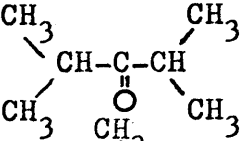
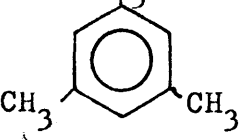
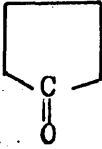
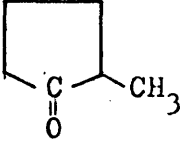
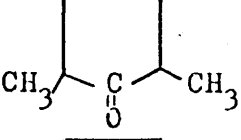
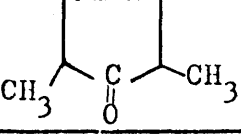
| Peak No. | Liquid Volatile | Mole % Yield of Liquid Volatile | | | |
|----------|---|---------------------------------|-------|-------|-------|
| | | LiPMA | NaPMA | KPMA | CsPMA |
| 1 | $\text{C}_2\text{H}_5\text{CHO}$ | Trace | Trace | Trace | Trace |
| 2 | CH_3COCH_3 | 1.26 | .6 | .2 | - |
| 3 | $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}-\text{CHO} \\ \diagup \\ \text{CH}_3 \end{array}$ | .74 | .6 | .3 | .3 |
| 4 | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CHO} \end{array}$ | 3.0 | 2.16 | 4.9 | 2.5 |
| 5 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ | 1.4 | 1.5 | 4.8 | 1.8 |
| 6 | $\begin{array}{c} \text{CH}_3\text{C}-\text{CH}_2\text{CH}_3 \\ \\ \text{O} \end{array}$ | 1.4 | 1.9 | 1.6 | .3 |
| 7 |  | Trace | Trace | Trace | Trace |
| 8 | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{C}-\text{CH}_3 \\ \\ \text{O} \end{array}$ | .3 | .4 | .3 | .5 |
| 9 | ? | Trace | Trace | Trace | Trace |
| 10 | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{O} \end{array}$ | .54 | .6 | 1.6 | .50 |
| 11 | $\begin{array}{c} \text{CH}_3-\text{CH}-\text{C}-\text{CH}_2\text{CH}_3 \\ \\ \text{O} \end{array}$ | 1.5 | 1.1 | 1.0 | .25 |

Table 4.6 (Continued)

| Peak No. | Liquid Volatile | Mole % Yield of Liquid Volatile | | | |
|----------|---|---------------------------------|-------|-------|-------|
| | | LiPMA | NaPMA | KPMA | CsPMA |
| 12 | ? | Trace | Trace | Trace | Trace |
| 13 | $\text{CH}_3\text{-CH=CH-CO-CH}_3$ | .54 | .5 | .3 | .26 |
| 14 |  | Trace | Trace | Trace | Trace |
| 15 |  | Trace | Trace | Trace | Trace |
| 16 |  | Trace | Trace | Trace | Trace |
| 17 | Mestyloxiide | Trace | Trace | Trace | Trace |
| 18 |  | Trace | .3 | .2 | .20 |
| 19 |  | 2.2 | 1.0 | .1 | Trace |
| 20 |  | 2.6 | .8 | Trace | .2 |
| 21 |  | 2.8 | 1.0 | .34 | .2 |
| Total | | 18.28 | 12.46 | 15.64 | 7.02 |

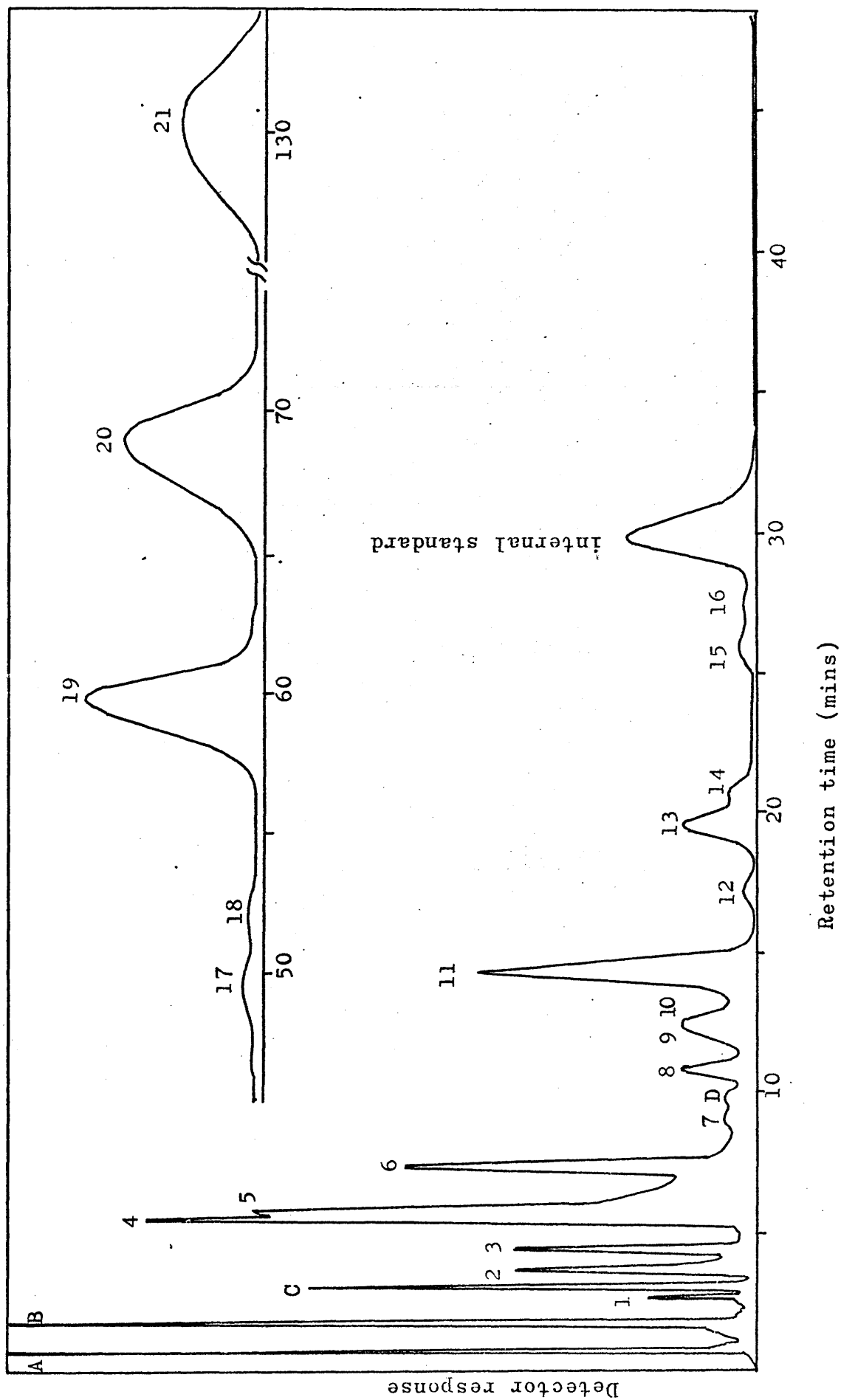


Fig. 4.13 GLC analysis of liquid degradation products of LiPMA, column temperature 60°C, helium carrier gas. 35 ml/min

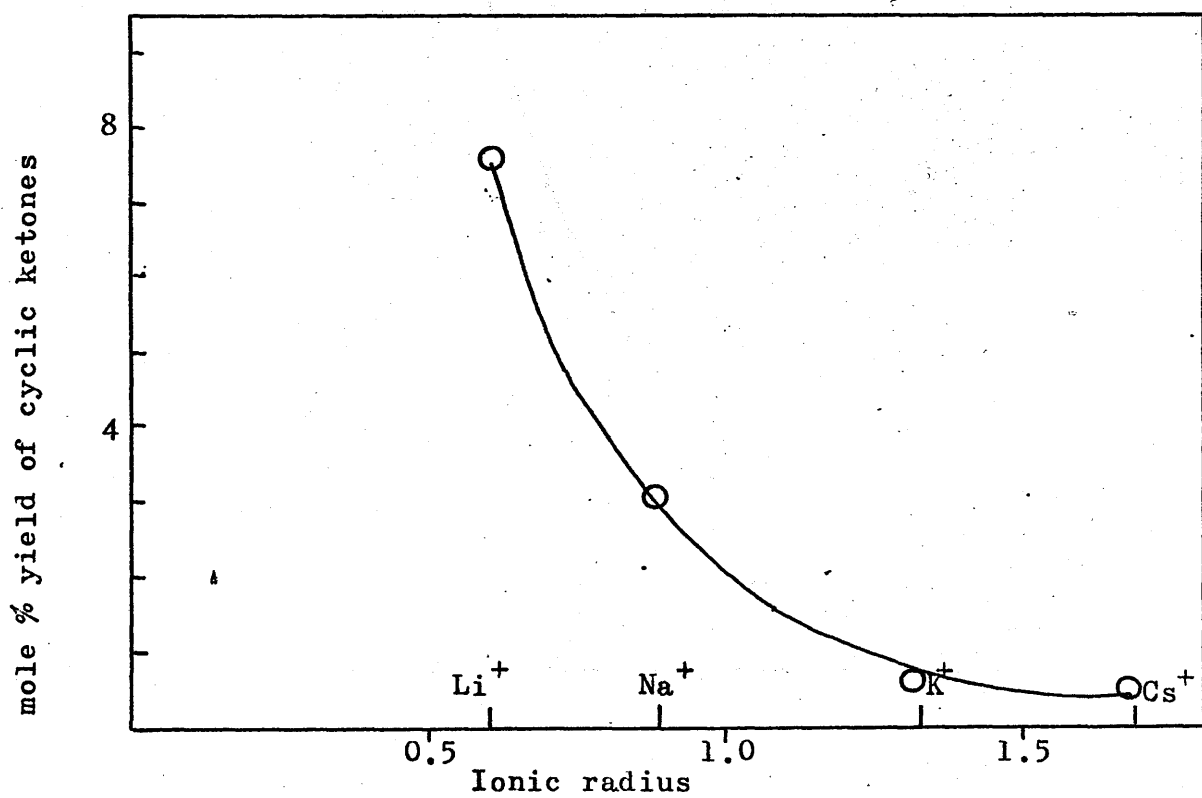


Fig. 4.14 Evolution of cyclic ketones versus ionic radius

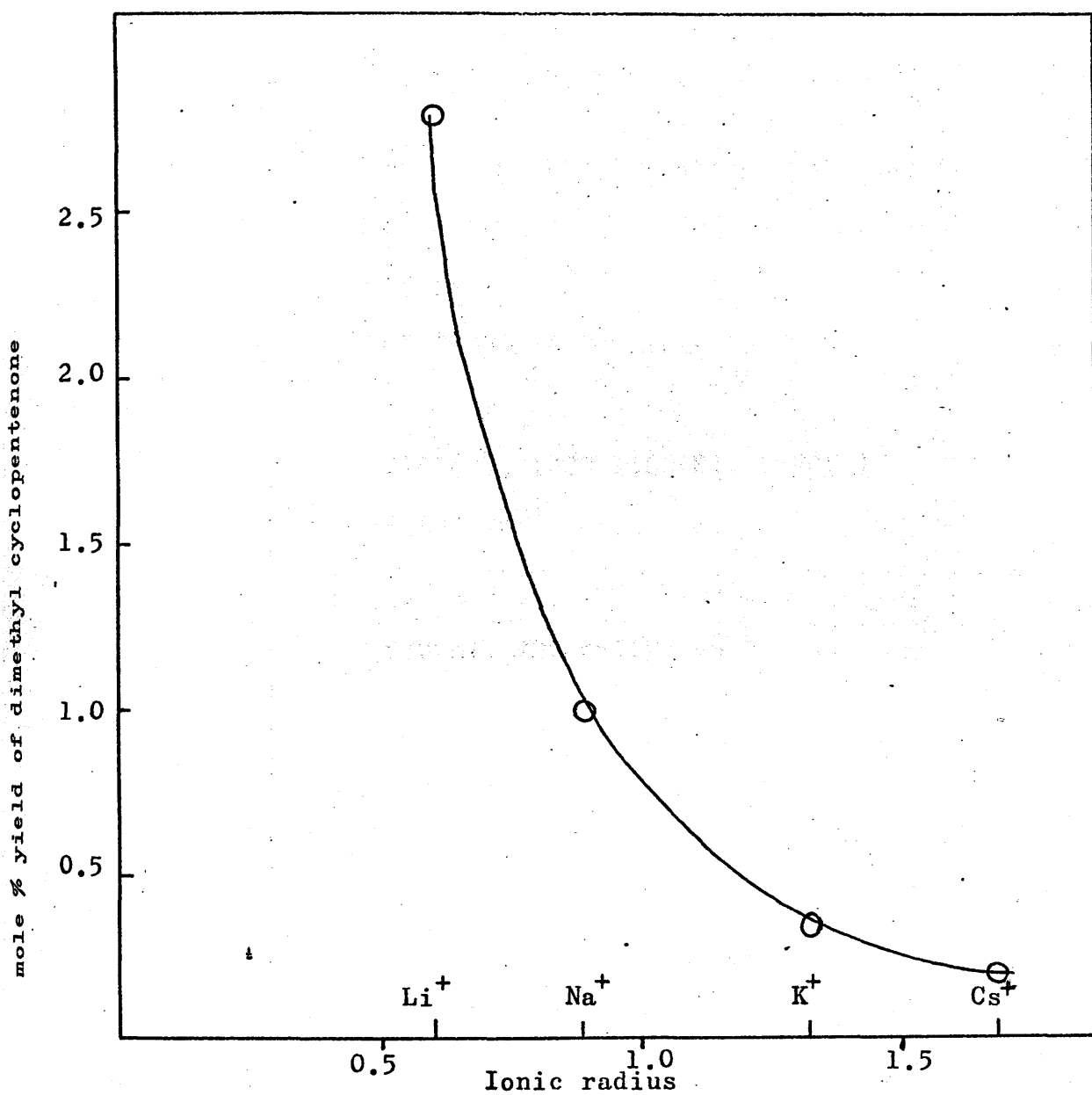


Fig. 4.15 Evolution of 2,5 dimethyl cyclopentenone
versus ionic radius

RESIDUE ANALYSIS

Investigations of the black residues obtained from the homopolymers, after degradation to 500°C, were undertaken by infra-red spectroscopy.

The main peaks found in the spectra were:-

1. LiPMA

2940(W), 2500(W), 1470-1500(S), 1090(m)
860(S), 740(W) cm^{-1}

2. NaPMA

1440(S), 870(m), 700-695(W) cm^{-1}

3. KPMA

3180(S), 1530(m), 1450-1360(b.S), 1070(W)
880(S), 700(m), 670(W) cm^{-1}

4. CsPMA

3180(S), 1560(S), 1450(S), 1380(S), 1060(m),
880(m), 705(m), 670(m) cm^{-1}

By comparison with standard spectra, this suggests that in all four cases the main constituents of the black residues are the respective metal carbonate and charcoal. A broad and small shoulder at 3200 cm^{-1} present in the case of NaPMA residue and strong bands at 3180, 1530-1560 cm^{-1} in the cases of KPMA and CsPMA residues suggest the presence of MHCO_3 , or the peak at 3180 cm^{-1} could be the OH stretch for MOH.

In order to observe the presence of metal oxides, the spectra were obtained down 200 cm^{-1} . Only the residue from LiPMA gave a broad band at 360-280 cm^{-1} and a little shoulder

at the same wave numbers in the case of NaPMA, but these peaks cannot be assigned strictly to oxides, as all the alkali metal carbonates give a strong broad band between 200 and 300 cm^{-1} . Bicarbonates and metal hydroxides cannot be regarded as genuine degradation products, because exposure of the residues containing metal oxides to the atmosphere could instantly convert them into bicarbonate, hydroxide, carbonate and possibly to some other ions, but the presence of metal carbonates was certain as further degrading the homopolymer residues up to 1000°C produced more CO_2 .

The presence of the metal in a form other than the carbonate was investigated in an indirect way, by titrating the metal ion in the residue as follows:-

An accurately weighed amount of homopolymer was degraded under vacuum to 500°C and the black residue was dissolved in 50 ml of 0.1M HCl with vigorous stirring and the solution was back titrated against 0.1M NaOH to the methyl orange end point. The amount of residue was estimated, from TGA of the homopolymer under vacuum, and not by weighing it in the TVA tube in order to avoid moisture absorbance by the residue on exposure to air. By knowing the volume of standard HCl used to neutralize carbonate in the residue, the percentage of the metal could be determined and hence the equivalent amount of carbonate can be calculated as exemplified in the case of NaPMA.

Wt. of polymer = 0.0581 gms

Wt. of black residue = 0.0296 gms (obtained by TGA as 51% residue)

Vol. of 0.1M HCl used = 7.1 ml

∴ No. of moles of Na = 7.1×10^{-4}

Now,

1 mole of Na \equiv 23 g (at Wt. of Na)

∴ 7.1×10^{-4} mole of Na $\equiv 7.1 \times 23 \times 10^{-4}$ gms

Now,

46 units of Na \equiv 106 units of Na_2CO_3

∴ $7.1 \times 23 \times 10^{-4}$ of Na $\equiv \frac{7.1 \times 23 \times 10^{-4} \times 106}{46}$ gms of Na_2CO_3

$\equiv 0.0375$ gms of Na_2CO_3 (If all the Na is present as carbonate)

However, the residue left at 500°C was 0.0296 gms; therefore, not all the sodium metal is present as carbonate. Certainly there are some other species like Na_2O and charcoal. Similarly the amount of observed residue for LiPMA was 50% and the calculated value with respect to the amount of lithium calculated, is 49.3%, this shows that Li_2CO_3 is the major constituent of the actual residue. This difference may be attributed to experimental error, as CO_2 in the titration mixture may have caused some complications as it always does. In the cases of KPMA and CsPMA, the calculated amount of residues are greater than the observed. These results should be treated cautiously as these cannot be used to interpret

the exact amount of all the constituents, but it does give some rough idea that there are some other species in the residues other than metal carbonates and whatever the % error may be, it is towards the negative as only excess HCl was back titrated against standard NaOH.

| Homopolymer | % residue (TGA) | 0.1M HCl (ml) | Calculated % residue (as M_2CO_3) | % difference |
|-------------|--------------------|------------------|--|-----------------|
| LiPMA | 50.0 | 8.1 | 49.3 | -0.7 |
| NaPMA | 51.0 | 7.1 | 60.9 | +9.9 |
| KPMA | 49.0 | 7.5 | 59.7 | +10.7 |
| CsPMA | 51.0 | 5.0 | 59.09 | +8.09 |

Table 4.7

ANALYSIS OF THE COLD-RING FRACTION

Infra-red spectra of the yellowish-white cold-ring fractions obtained from the four homopolymers after degradation to 500°C at the rate of 10°C/min, were run by using KBr discs and the regions of interest (for LiPMA, NaPMA, KPMA and CspMA) are shown in Figs. 4.16 and 4.17. The quantitative yield of cold-ring fraction was determined by weighing the TVA tube clean, and then containing the cold-ring fraction; the weight % yield is given in Table 4.8.

It can be seen that IR spectra of the cold-ring fractions are similar to that of monomer. For LiPMA, the peaks at 1577-1508 and 1430 cm^{-1} are due to asymmetric and symmetric stretching modes of the $-\text{CO}_2^-$ group. These peaks are present both in lithium methacrylate and lithium isobutyrate as shown in Fig. 4.16. Other bands at 1240, 1008, 858, 845 and 770 cm^{-1} all belong to the monomer. From the reference spectrum of lithium methacrylate, it appears that bands at 845 and 858 cm^{-1} are of the same intensity but in the cold-ring spectrum, they are not, showing the presence of another compound which absorbs at 845 cm^{-1} . The presence of double bond peaks at 1640 cm^{-1} in LiPMA and NaPMA cold-ring fraction spectra is not clearly seen, since there is only a small amount of monomer present, compared with other species in the cold-ring fraction. The lack of appearance of a peak at 1640 cm^{-1} in the sample may have been masked by the presence of moisture which also absorbs in this region, but the double bond peak becomes more apparent in the case of

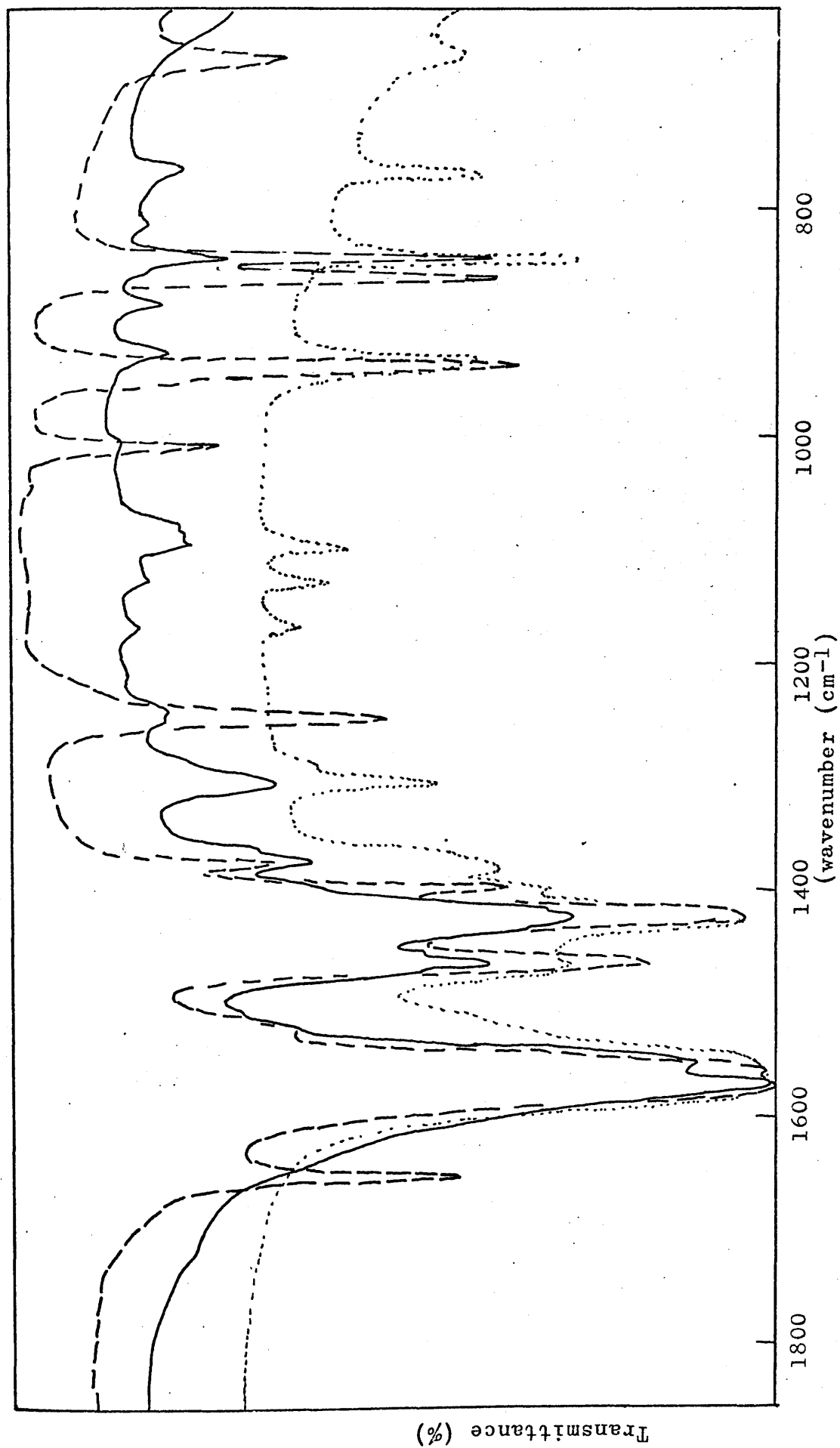


Fig. 4.16 IR absorption spectra of: — CRF of LiPMA, --- LiMA and lithium isobutyrate

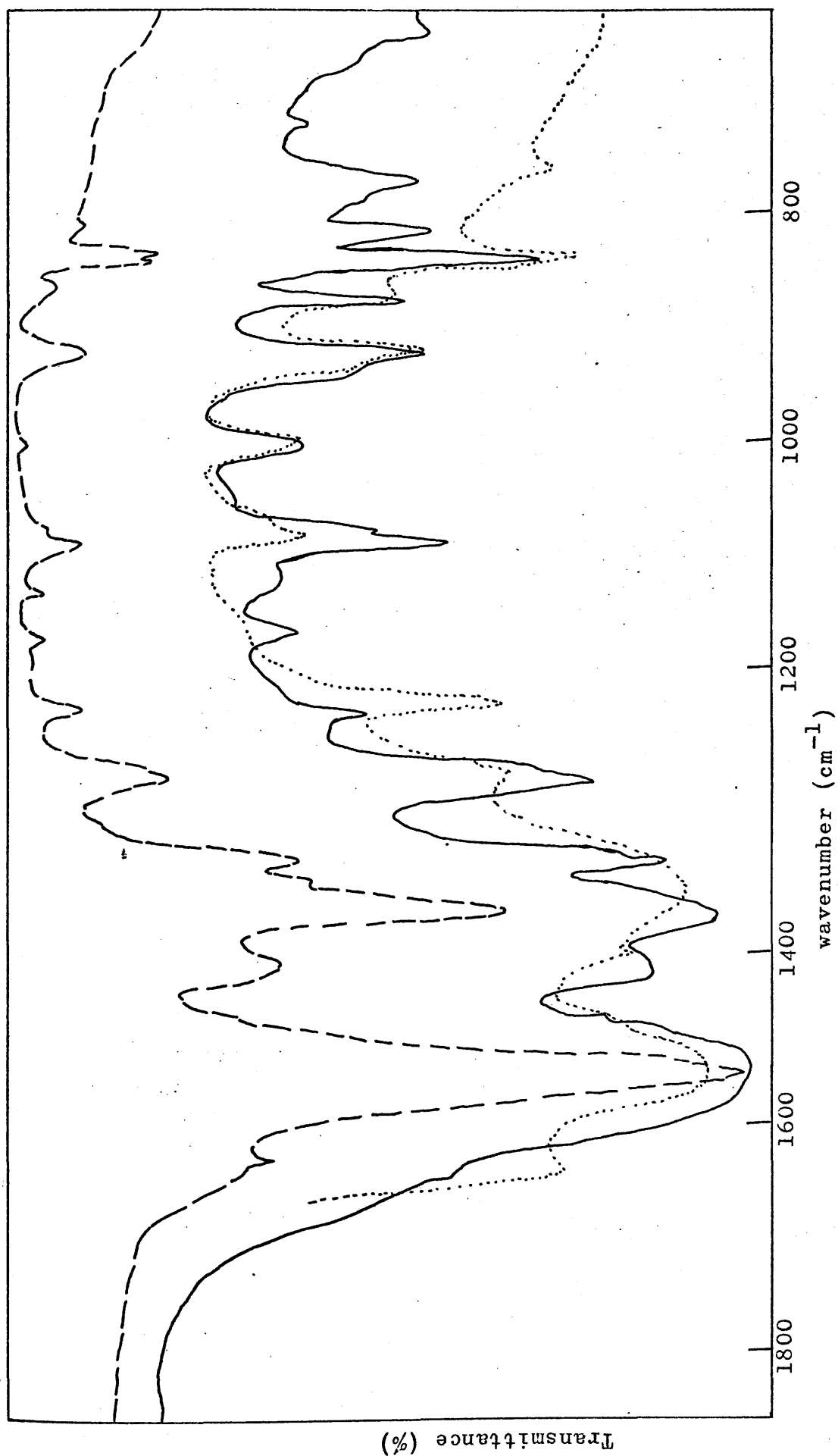
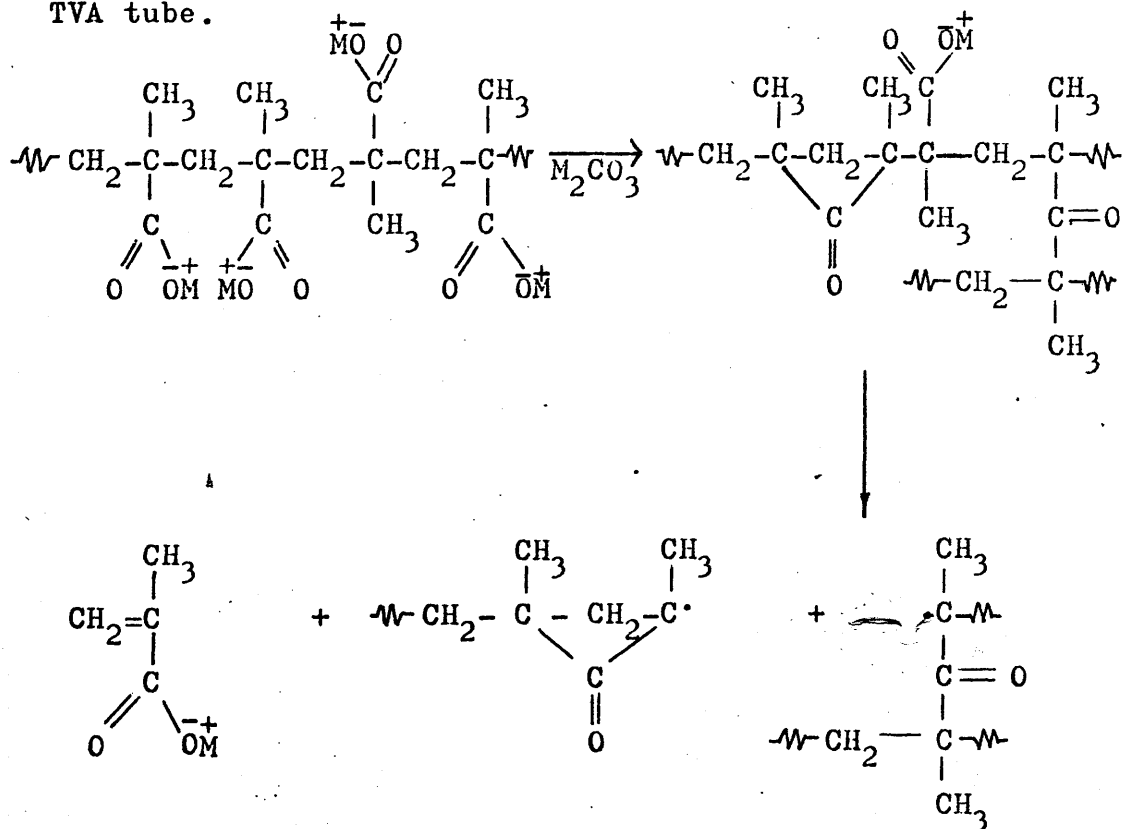


Fig. 4.17 IR absorption spectra of CRF; — NaPMA, --- KPMA and -.-.- CsPMA.

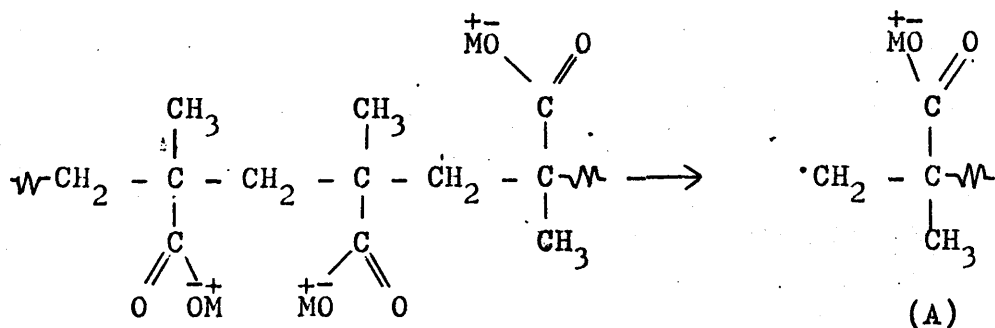
KPMA and CsPMA cold-ring fractions. This indicates that the production of monomer increases as the size of the ion increases, which is again quite in agreement with the previous statements about the tacticity of the homopolymers. Due to the increase in syndiotacticity of the homopolymer with the size of metal ion, the chances of leaving unreacted monomer units during degradation, become more probable and trapped monomer units may escape to the cold-ring of the TVA tube.



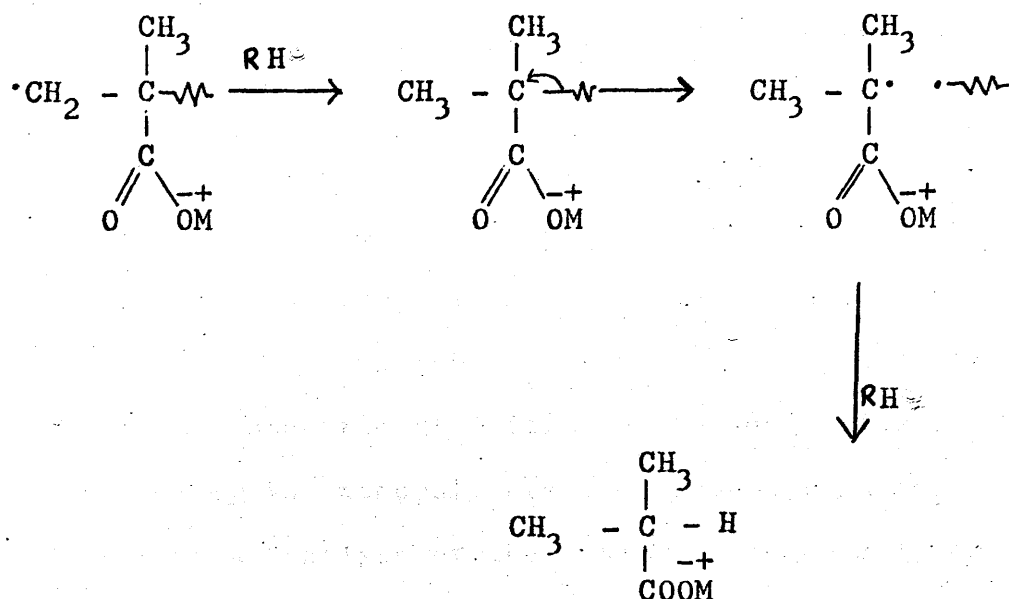
The relative amounts of monomer produced cannot be determined since a fraction of it may decompose at the base of the tube as it leaves the chain.

Other peaks found in the infra-red spectra of cold-ring fractions of homopolymers, were at 1310, 1170, 1120, 1100, 940, 845 and 770 cm^{-1} . These frequencies are in good agreement with those of the reference spectra of metal isobutyrate as shown in Fig. 4.16. Only the three weak bands at 1090, 888 and 820 cm^{-1} do not correspond either to monomer or isobutyrate spectra.

The formation of metal isobutyrate could be considered in the same fashion as in the case of monomer, except for the hydrogen abstraction.



The free radical (A) is produced at a higher temperature, therefore it either splits to monomer or abstracts hydrogen and tends to form isobutyrate.



An alternative pathway is that isobutyrate could also form by the reduction of monomer, but energy consideration and the reactivity of the free radical favour the former suggestion.

| Homopolymers | LiPMA | NaPMA | KPMA | CsPMA |
|---------------------------------------|-------|-------|------|-------|
| Wt. percentage of cold-ring fraction. | 29.5 | 31.7 | 35.5 | 40.2 |

Table 4.8

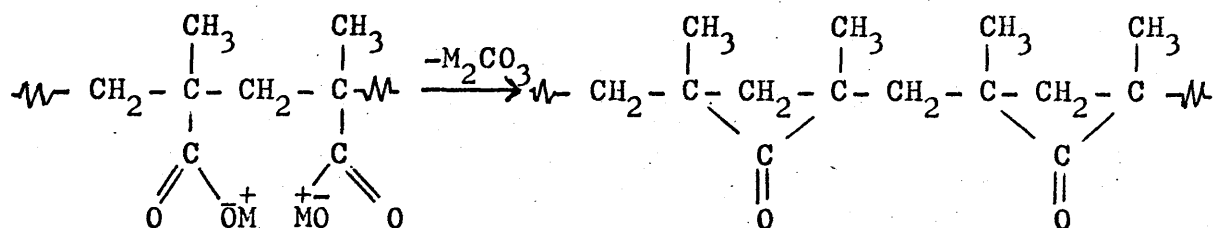
Quantitative yield of cold-ring fraction

STRUCTURAL CHANGES DURING DEGRADATION

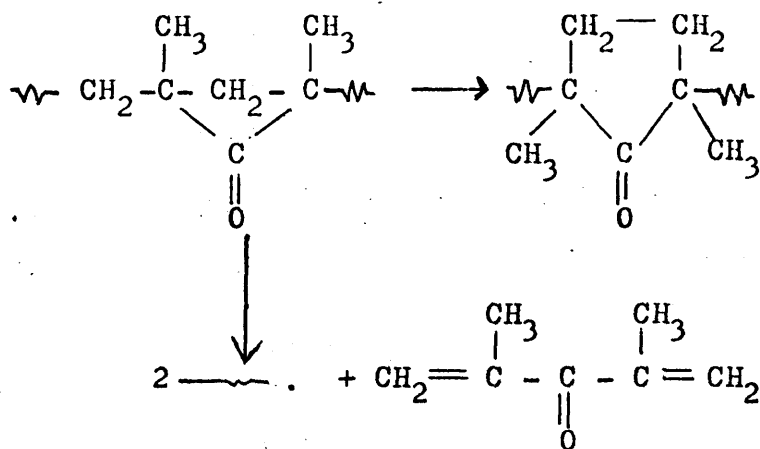
A 50 mg sample of each alkali metal polymethacrylate was degraded at 10°C/min to 350°C, cooled and extracted with methanol. The soluble portion of the residue was precipitated in ether and infra-red spectra obtained as KBr discs. It was found that the soluble part of the residue had the same infra-red spectrum as the insoluble part and both of these were similar to the spectrum of initial undegraded polymer.

Originally the homopolymers are insoluble in methanol and the fact that a fraction of the residue becomes soluble after heating to 350°C can be explained if the process occurring is merely chain scission to yield fragments of identical structure, but with a much lower molecular weight.

A 50 mg sample of each homopolymer was degraded isothermally to 400, 420, 450°C for half an hour under similar conditions and the spectra of the residues obtained as KBr discs. The region of interest is shown in Fig. 4.18. It is obvious from these spectra that the band at 1210 cm^{-1} is decreasing in intensity and new bands start appearing at 1470, 1090 and 860 cm^{-1} . These peaks are in agreement with the spectrum of the metal carbonate. Another new broad band appears at 1300 cm^{-1} , which is present in the metal isobutyrate spectrum, showing the presence of a trace of this compound. The formation of metal carbonate suggests that a ketonic structure should be formed, and the $\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-}$ frequency should appear in the region of 1750 cm^{-1} , but as it is clear from Fig. 4.15, there is no such band present.



In the above scheme, the formation of carbonate leaves a di-radical species which transiently forms a cyclobutanone ring; however the ring strain involved is too great, and so immediately either hydrogen transfer occurs to form cyclopentanone groups or ring cleavage occurs to form aliphatic ketones.



If the cyclopentanone rings are formed by the rearrangement of cyclobutanone ring in the chain then the IR spectrum should show a strong band at $\approx 1740\text{ cm}^{-1}$. The absence of this band indicates that these cyclic structures only appear in the volatile reaction products.

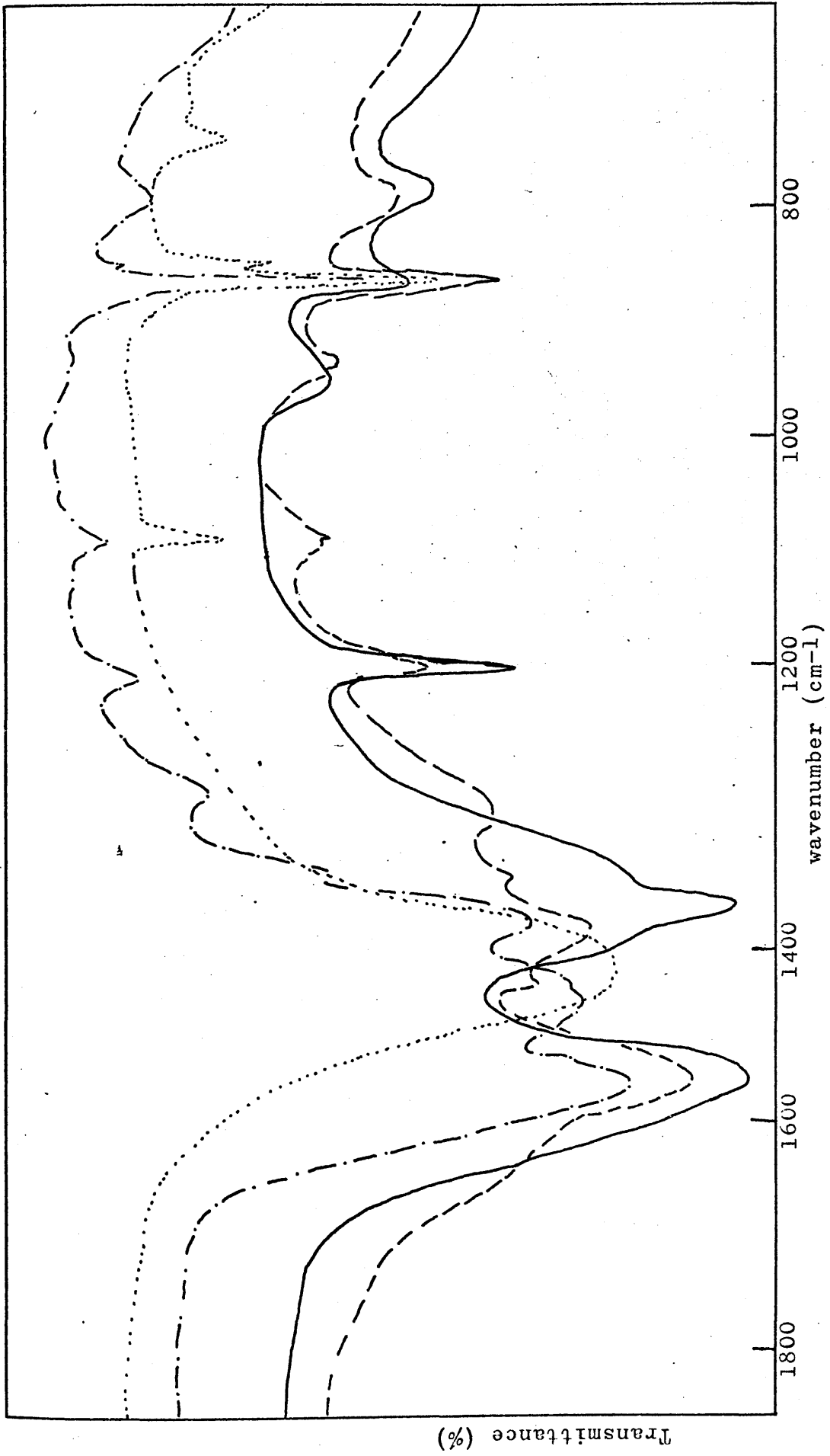
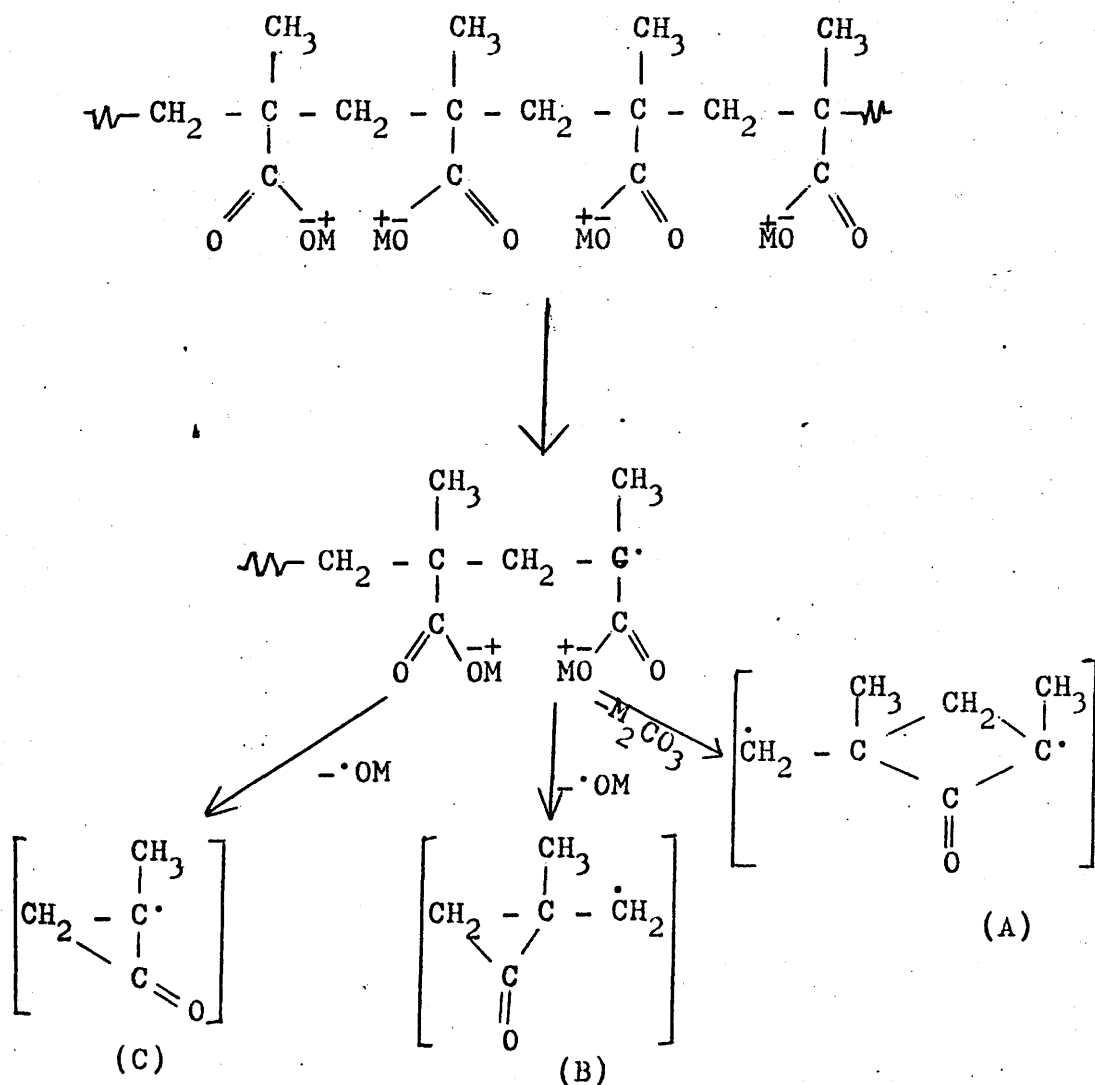


Fig. 4.18 IR absorption spectra of: — KPMA, --- KPMA degraded at 400°C, - · - · KPMA degraded at 420°C and KPMA degraded at 450°C for 30 mins.

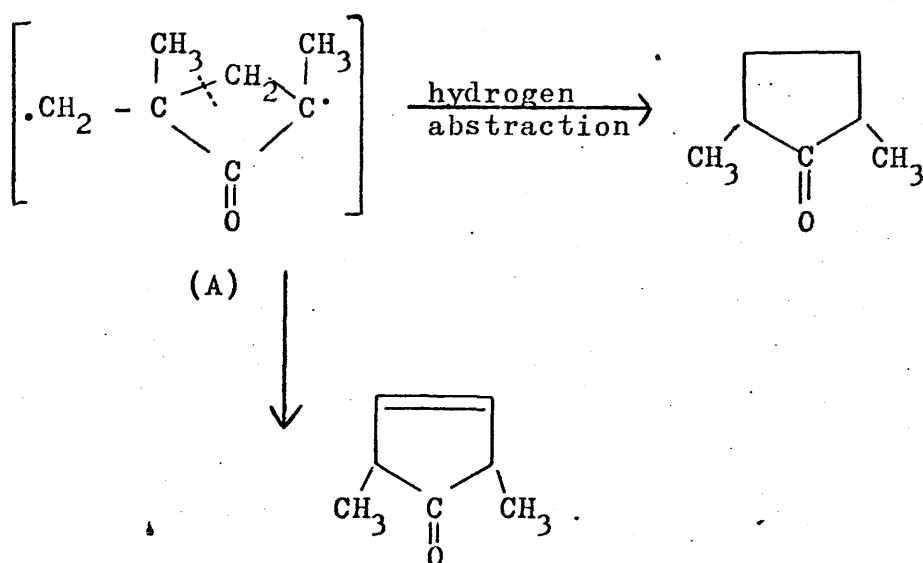
PROPOSED REACTION MECHANISM IN ALKALI METAL POLYMETHACRYLATES

The reaction mechanism shown below has been put forward to account for the major degradation products evolved from the four homopolymers. The experimental data and the results can lead to the postulation of three parallel degradation processes, depending on whether or not carbonate formation precedes chain scission.

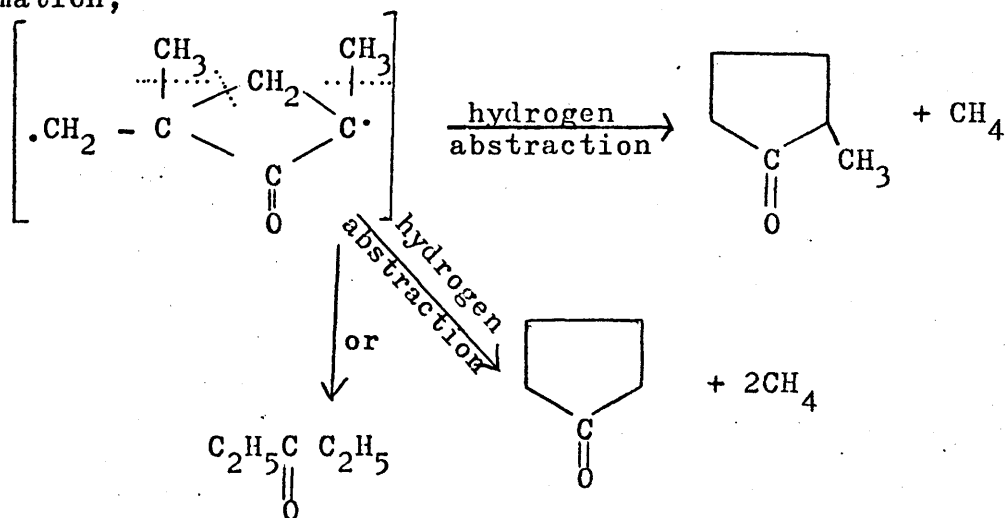


These three possible transient forms could lead to the formation of different compounds. As these are formed at very high temperature, therefore the reactivity of these radicals would be very high and they would abstract hydrogen readily.

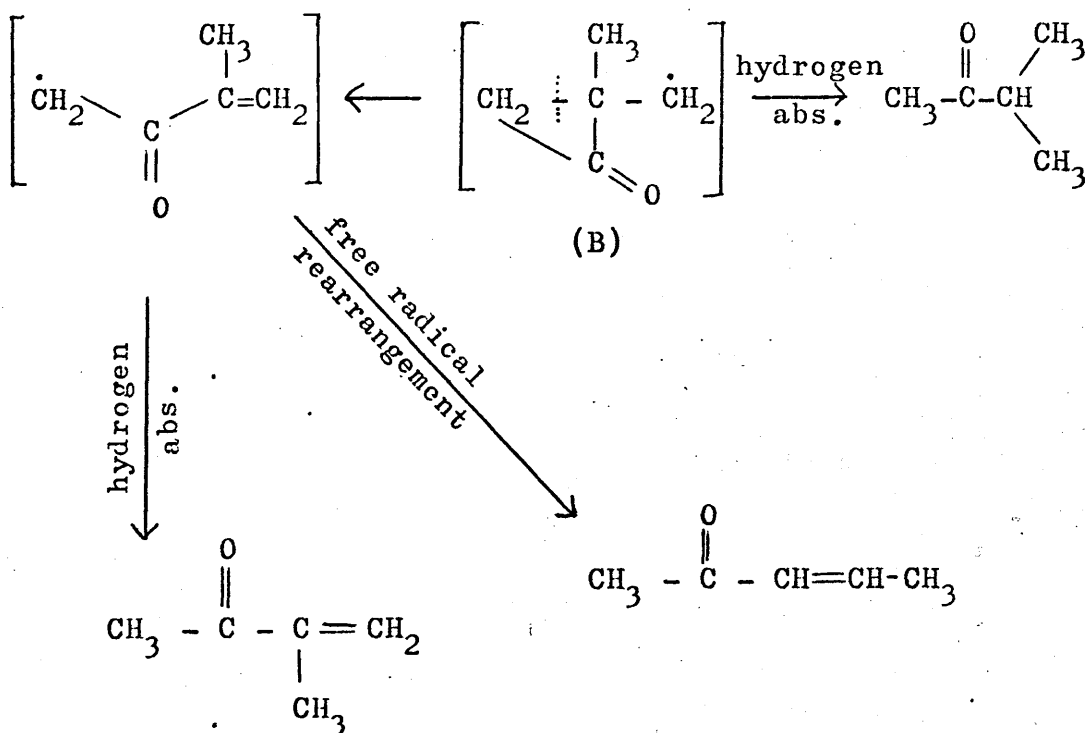
The formation of cyclic ketones and diethyl ketone can be explained on the basis of transient form A;



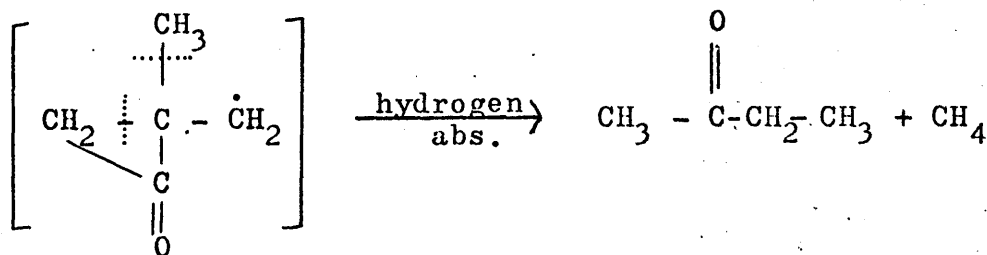
Also with loss of $\text{CH}_3\cdot$ as methane prior to cyclic ketone formation;



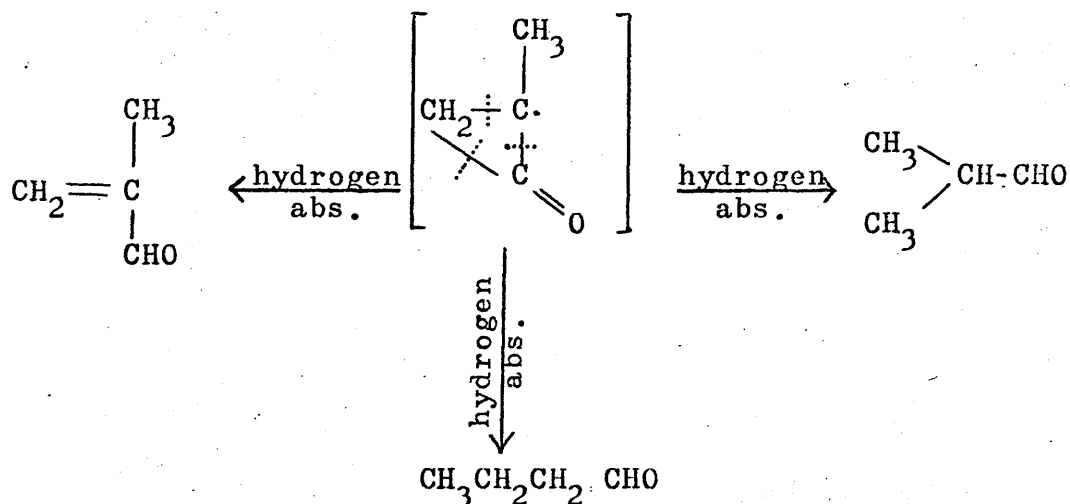
The formation of methylisopropyl ketone, methyl n-propenyl ketone, methyl isopropyl ketone and methylethyl ketone can be postulated from the transient state (B);



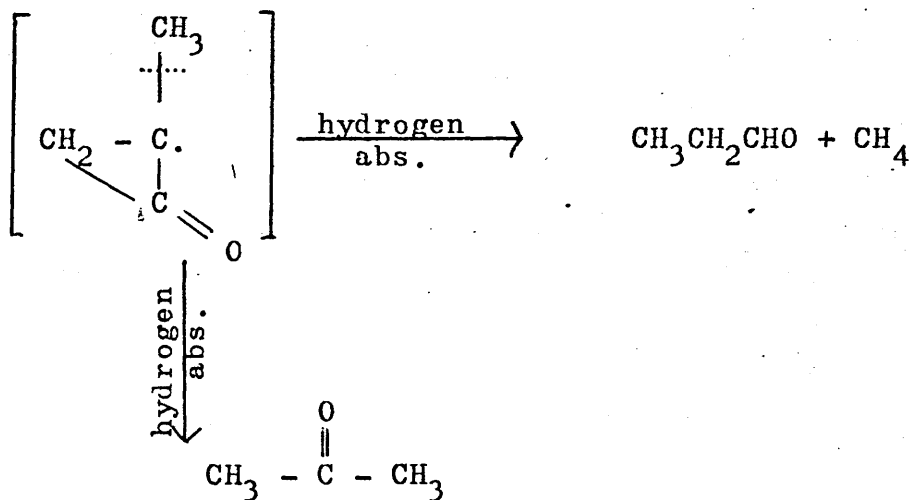
Also with prior loss of the methyl group;



The transient state (C) could lead to the formation of aldehydes and acetone as;



and again methane loss is possible prior to product formation;



The formation of isobutene, propylene and carbon monoxide could be the result of loss of a CO radical prior to the ketone formation in all three transient states.

Toluene, benzene and mesitylene obtained as minor constituents in their relative amounts might not be derived through the above mechanism.

CHAPTER FIVE

THERMAL DEGRADATION OF ALKALINE EARTH METAL SALTS OF POLY-METHACRYLIC ACID

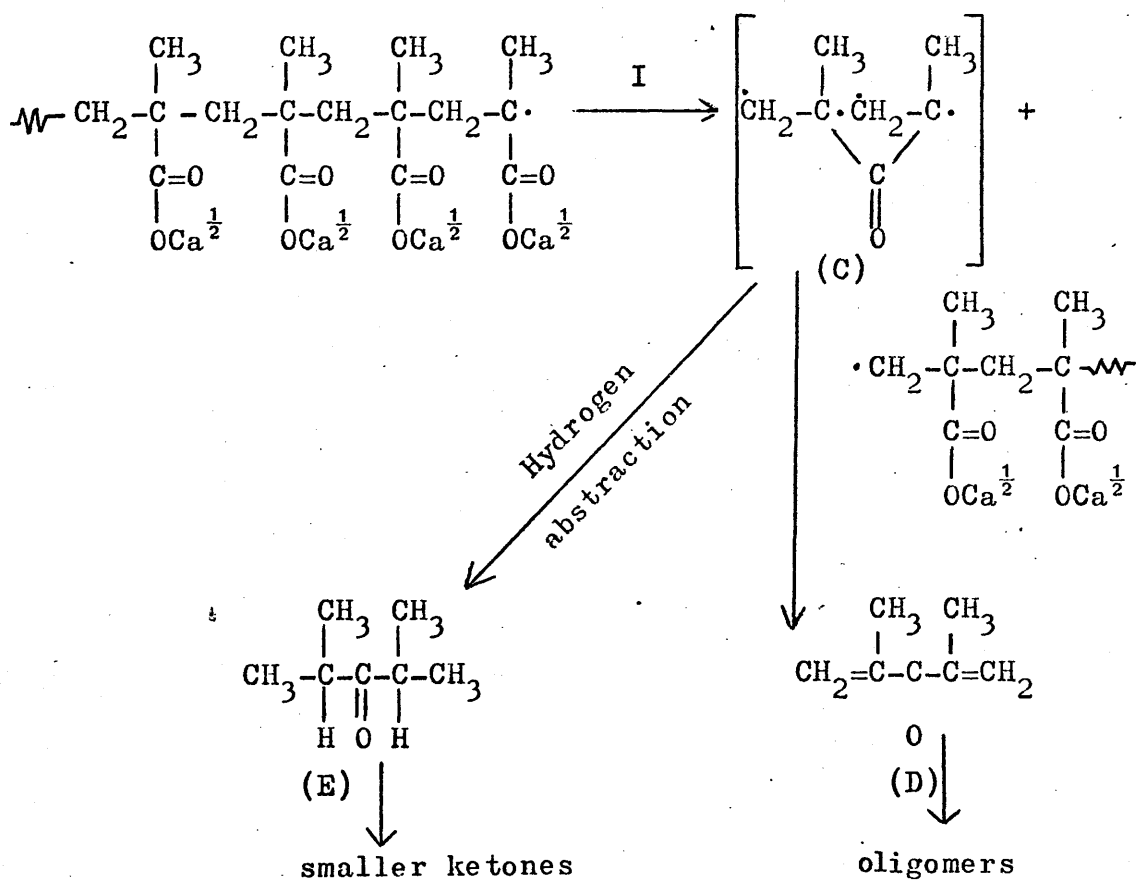
Thermal degradation of alkali metal salts of polymethacrylic acid which have one methacrylate unit per metal atom has been discussed in the preceeding chapter. Degradation of the divalent metal salts which have two methacrylate units per metal atom is described in this chapter. There is a similarity in the thermal behaviour of the monovalent and divalent metal salts but an appreciable difference exists in the relative amount of volatile products. This chapter considers the degradation of Mg, Ca, Sr and BaPMA and a further comparison will be made with ZnPMA in the next chapter.

INTRODUCTION

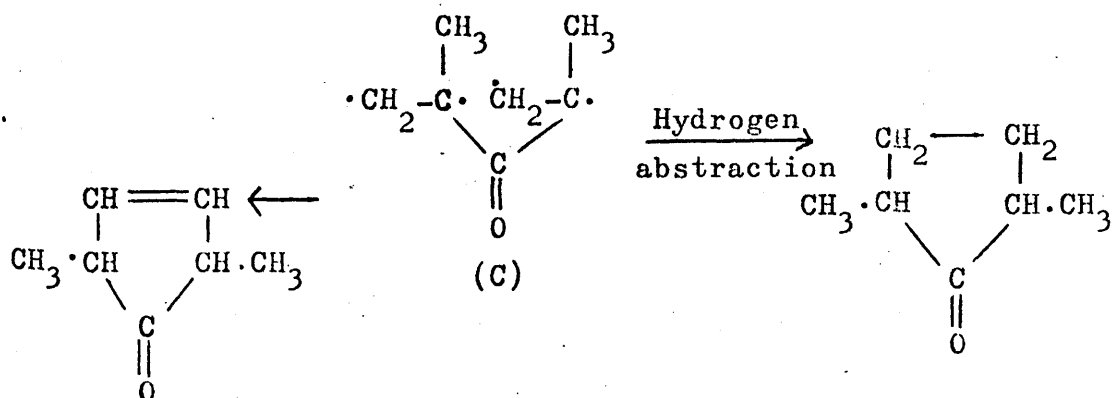
Shu Furukawa and co-workers^{37,88} were the first to carry out the dry distillation of calcium and barium polymethacrylate. They reported only one liquid degradation product, namely, 2.5 dimethyl-3-cyclopentene-1-one. In their latter reviews^{38,39,40} they reported ten different ketones from the degradation of CaPMA at temperatures from 35° to 45°C. Furukawa et al.,⁸⁹ degraded isotactic and atactic CaPMA and found that the volatile products were similar in nature, but different in their relative amounts. They have suggested that the thermal degradation behaviour of CaPMA was similar to those of PMMA

and PMA, such that chain scission might be assumed to proceed by the same mechanism. They postulated the following courses:-

A. major chain scission may occur through a radical depolymerization mechanism, unzipping to monomer-type constituents,



B. As I but with successive cyclization.



The above mechanism is open to contention since

(a) The transient species (C) with four free radical sites, formed in the temperature range 350°-450°C, appears far too unstable to go through a systematic formation of volatile products.

(b) Methylcyclopentanone, cyclopentanone, methylethylketone, diethylketone, methyl isopropyl ketone and methyl n-propenyl ketone cannot be derived by this mechanism. Furukawa³⁸ himself has admitted this discrepancy in his proposed mechanism but claimed that di-isopropyl and di-isopropenyl ketones (E,D) gave rise to smaller ketones and oligomers. This does not seem to be the case, as in the present study, these higher ketones were passed through the TVA tube at 500°C under normal TVA conditions and no degradation to smaller ketones was observed.

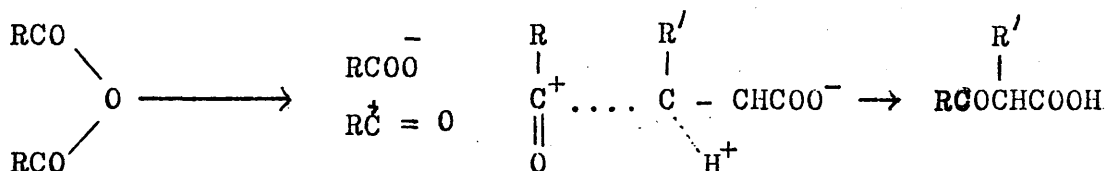
(c) The size of the sample degraded was between 100-200 g. This would appear to be too large since there is no guarantee that the temperature throughout the sample would rise uniformly and there is also afforded the possibility of secondary reaction, involving radical species diffusing through the bulk of the sample.

(d) The calcium polymethacrylate studied by Furukawa et al.³⁸ was synthesised from the reaction of CaCl_2 on aqueous NaPMA, obtained by saponification of polymethylmethacrylate. This reaction is not homogeneous, as CaPMA is insoluble in the reaction mixture. This process of obtaining CaPMA will result in the formation of a terpolymer containing CaMA, NaMA and MMA

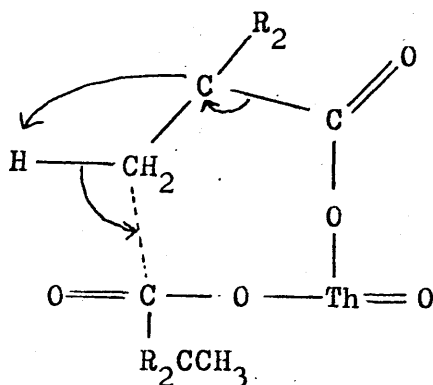
units in the chain. Furukawa et al.³⁸ have also admitted this irregularity in the polymer studied, since methanol was obtained as a product. They explained the production of methanol by considering the degradation of a mixture of CaCl_2 and PMMA under the same conditions and temperature used for CaPMA. Apart from methanol, they also identified methylethyl ketone, MMA and MA from the degradation of this mixture. Thus, a sample of CaPMA prepared by the above method will give rise to many different routes of degradation. Before discussing the results obtained in the present investigation, it seems appropriate to discuss the ketonic decarboxylation of divalent metal salts of aliphatic acids.

There has been a great deal of work carried out on the mechanism of ketonic decarboxylation, but in spite of this, only a few definite conclusions can be reached. The first mechanistic proposal was probably that of Bamberger⁹⁰, who suggested the anhydride as an intermediate. This seems quite likely in the case of cyclic ketones, since cyclopentanone and cyclo hexanone may be prepared in 50% yield by merely distilling adipic and pimelic acids at atmospheric pressure with excess acetic anhydride.⁹¹ Shemyakui⁹² found that passage of acetic anhydride over CaO gave acetone at 350°C while calcium acetate did not decarboxylate until 400°C . Koch and Leibritz⁹³ interpret the decarboxylation of anhydride in terms of the β -keto acid intermediate, first proposed by Neunhoeffer and Paschke⁹⁴. The former author noted that while carboxylate salts should not lose an α -hydrogen readily (since this would form a doubly

charged anion), loss of a proton from a carbon and to the electron withdrawing anhydride group should be fairly easy. Thus in fact the formation of β -keto acid should take place by the dissociation of anhydride into acylium and carboxylate ions, followed by attack of acylium ion on the α -carbon of the carboxylate with a transfer of a proton,



Neunhoeffer and Paschke⁹⁴ proposed the intermediacy of a β -keto acid on the basis that only those acids which possess an α -hydrogen readily undergo ketonic decarboxylation. Branched-chain aliphatic acids give poorer yields than straight chain acids. Such a mechanism was extended further by Whitmore,⁸² Miller and Cook, who studied the pyrolysis of trimethyl acetic acid over aerogel thoria at 490°C. The products were as follows. $(\text{Me}_3\text{C})_2\text{CO}$ - none, $\text{Me}_3\text{C}\cdot\text{CO}\cdot\text{CH}_2\text{Me}_3$ -15%, $\text{Me}_3\text{C}\cdot\text{COMe}$ -9%, CO_2 -20%, CO -2.7%, $\text{Me}_3\text{C}\cdot\text{CHO}$ -3%, hydrocarbon-8% and starting material-21%. Whitmore claimed that this multiplicity of products arises from decomposition of $\text{Me}_3\text{C}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{Me}_2$, which in turn results from decarboxylation of a δ -keto acid, formed by a concerted mechanism involving a cyclic seven membered transition state.



R = an alkyl group

The above mechanism also suggests that branched-chain acids containing α -hydrogen octane may form both β - and - keto acids. O'Neill and Reed,⁸³ however, consider that multiplicity of products is not the result of decomposition of the expected parent ketone, but that a free radical mechanism is involved in which a branched-chain alkyl radical rearranges to a straight chain one. This free radical mechanism was further supported by Reed and Bell,⁸⁴ who studied the pyrolysis of barium acetate, using a tracer technique. Their results and mechanism are discussed in the preceeding Chapter. This free radical mechanism also seems consistent with present studies of salts of polymethacrylic acid. In the present investigations, when di-isopropyl ketone, 2,5-dimethyl-3-cyclopentene-1-one and 2,5-dimethyl 3-cyclopentanone were passed through the TVA tube at 500°C, under normal TVA conditions, no new materials were produced; this seems consistent with the mechanism of O'Neill and Reed.

EXPERIMENTAL

The preparation and history of the polymer used in this section, have been given in Chapter 3.

RESULTS AND DISCUSSION

All polymer samples studied were in the powder form and the polymer weight described in this section refers to the pure sample (anhydrous). The water contents were determined by TGA.

THERMAL VOLATILIZATION ANALYSIS

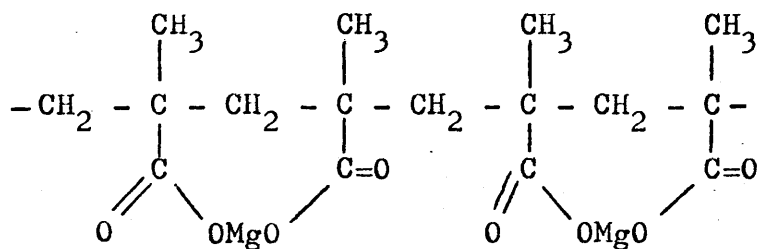
The sample size was 60 mg for each homopolymer. The polymer samples were degraded to 500°C at a heating rate of 10°C/min, under normal conditions of TVA. The TVA traces of MgPMA, CaPMA, SrPMA and BaPMA are reproduced in Figs. 5.1, 5.2, 5.3 and 5.4 respectively. The slow release of volatile material beginning at 100°C, is due to the release of water absorbed by the polymer. In the case of MgPMA, the reaction begins at about 280°C and gives a first peak maximum (T_{\max}) at 390°C. After the first peak, a more extensive release of volatile material begins and gives a second peak with T_{\max} at 442°C. After the second peak maximum the pirani response decreases rapidly in the case of MgPMA, but this becomes gradual in the cases of CaPMA and SrPMA and appears as a peak in the case of BaPMA.

First peak. It is obvious from the TVA traces of all the homopolymers that the area enclosed by the first peak, decreases as the size of metal ion increases and it diminishes completely

Second peak. In the second peak, divergence of the traces shows that some high boiling material is evolved at this stage of degradation. Cyclic and high boiling aliphatic ketones are noncondensable at 0° and -45°C but are condensable at -75°C in the TVA apparatus and thus there must be other products evolved, which are noncondensable at -100° and -196°C , and were probably carbon monoxide and methane. The separation of -100° and -196°C also suggests that low boiling materials are produced during degradation. The area enclosed between 0° ; -45° and -75°C may be accounted for by the evolution of high boiling ketones and as this area is decreased from Mg to BaPMA, this leads to the suggestion that the amount of cyclic ketones produced decreases as the size of the metal ion increases. Cyclic ketones can only be produced from the eight membered cyclic rings in the chain and are unlikely to arise from the cross-linked chain. Crosslinking is expected more in BaPMA than in MgPMA, as the metal ion size plays an important part in determining the polymer chain formation.

Third peak. From TVA trace of MgPMA, it is clear that after the second peak maximum, the traces start coming to the base line, but slowly in the cases of CaPMA and SrPMA. This slow release of products appears as another peak in the trace for BaPMA at a temperature of 465°C . Product analysis of this latter part of the traces showed that mainly carbon monoxide, carbon dioxide, methane and traces of aliphatic and cyclic ketones were present. This may also imply that crosslinked units are decomposing at a higher temperature and these units

in the case of BaPMA. A possible explanation is that the percentage of isotactic sequences in the polymer decreases with increasing size of metal ion. One would expect the isotactic segments to be degraded at lower temperature than syndiotactic segments in the chain, because in the case of isotactic



isotactic segments

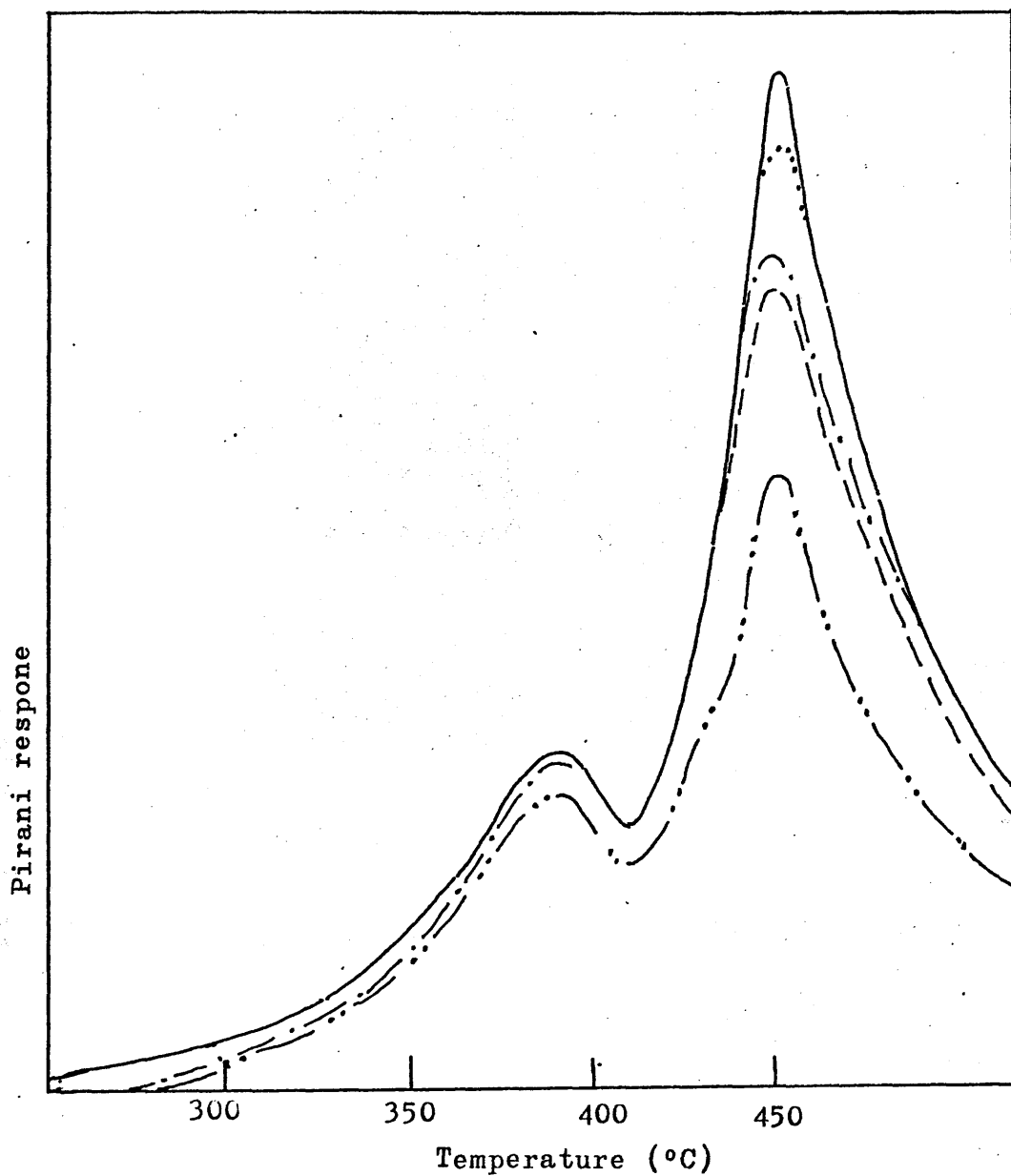
structure, there would be large strain on the polymer chain, having eight membered cyclic rings on one side. On the other-hand, in the case of syndiotactic segments, the strain would be in balance and hence the polymer would become more stable. There is no data available on the tacticity of divalent metal salts of polymethacrylic acid but analogous monovalent salts do behave in the fashion that syndiotacticity increases with the increasing size of metal ion and this has been discussed in Chapters 1 and 4. From TVA traces it is also clear that little divergence of traces occurs in the first peak suggesting that the products are almost entirely noncondensables at -196°C . Further identification by IR analysis showed that dimethyl ketene, methane, carbon monoxide, carbon dioxide and traces of acetone, methyl ethyl ketone and methacrolein, were the products of first peak.

| Homopolymer | T base °C | I Peak T max °C | II Peak T max °C | III Peak T max °C |
|-------------|--------------|-----------------------|------------------------|-------------------------|
| MgPMA | 284 | 390 | 442 | - |
| CaPMA | 355 | 408 | 454 | - |
| SrPMA | 320 | 408 | 454 | - |
| BaPMA | 386 | - | 454 | 465 |

Table 5.1

Details of TVA thermograms

- Figures 5.1-5.4



Trap Temp. °C

— 0

..... -45 where not co-incident with 0° trace

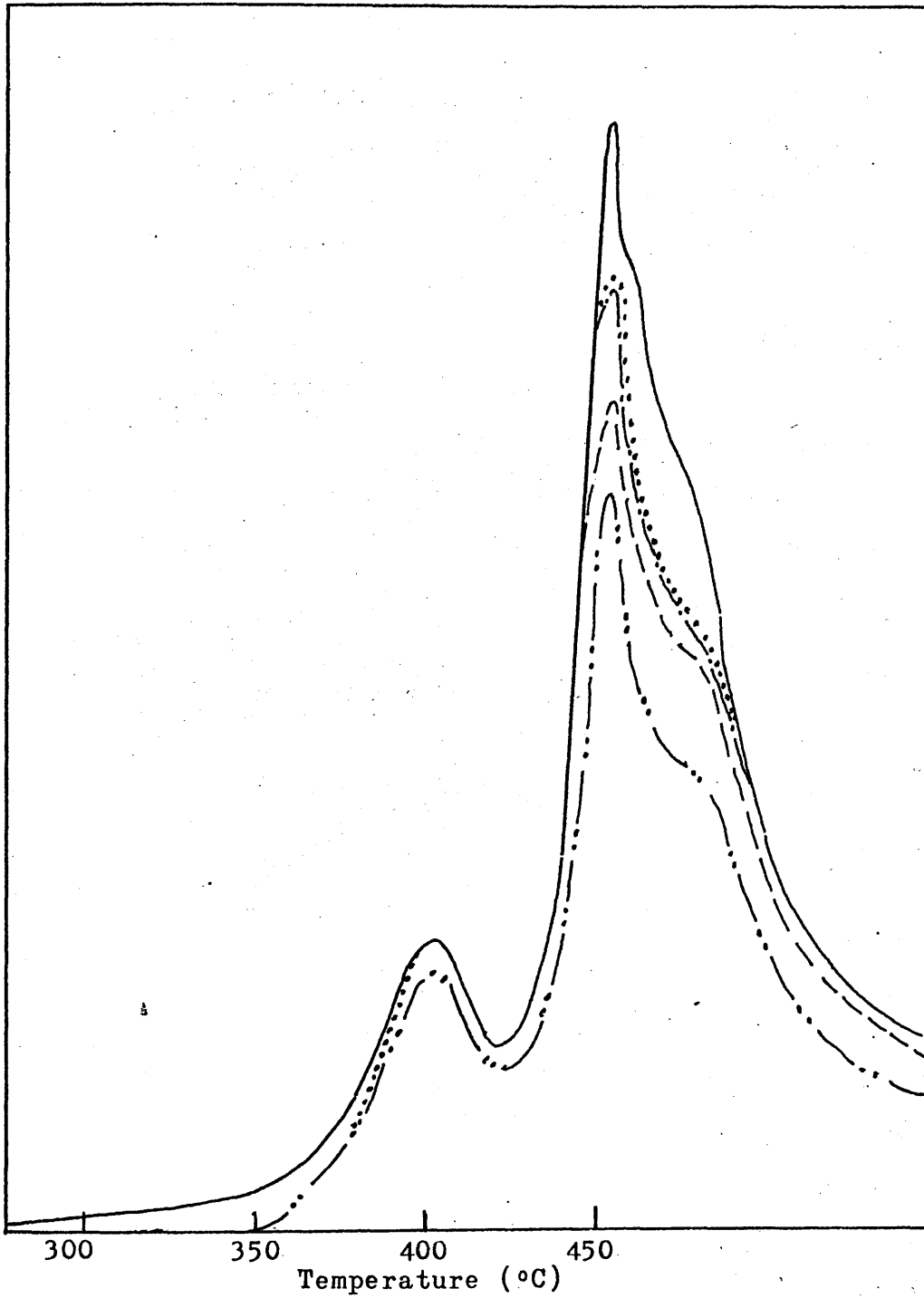
--- -75 where not co-incident with 0 and -45° traces

--- -100 where not co-incident with 0, -45 and -75° traces

--- -196

Fig. 5.1 TVA curve for MgPMA

Pirani response



Trap Temp. °C

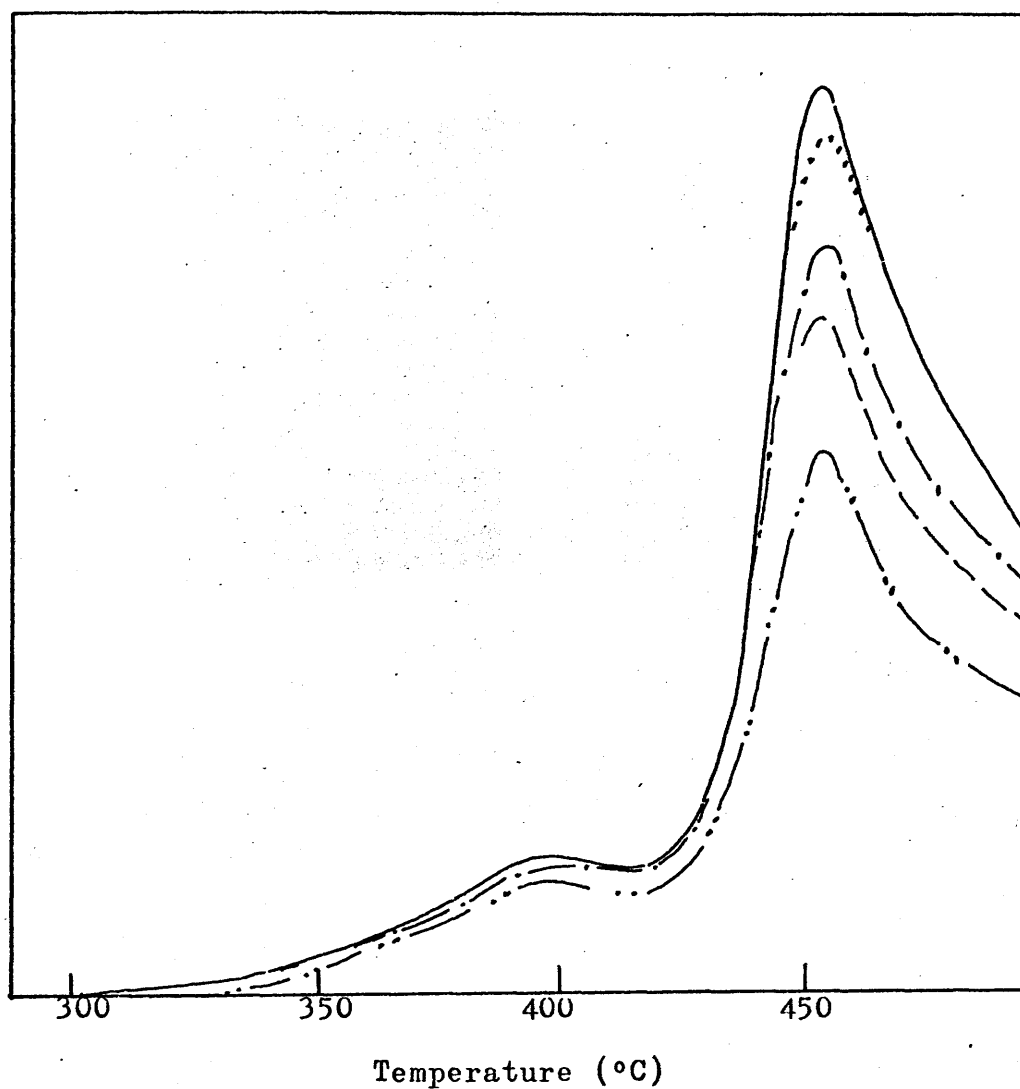
— 0

..... -45 where not co-incident with 0° trace

- - - - -75 where not co-incident with 0 and -45
traces.- - - -100 where not co-incident with 0, -45 and
-75° traces.

- - - -196

Fig. 5.2 TVA curve for CaPMA



Trap Temp. °C

— 0

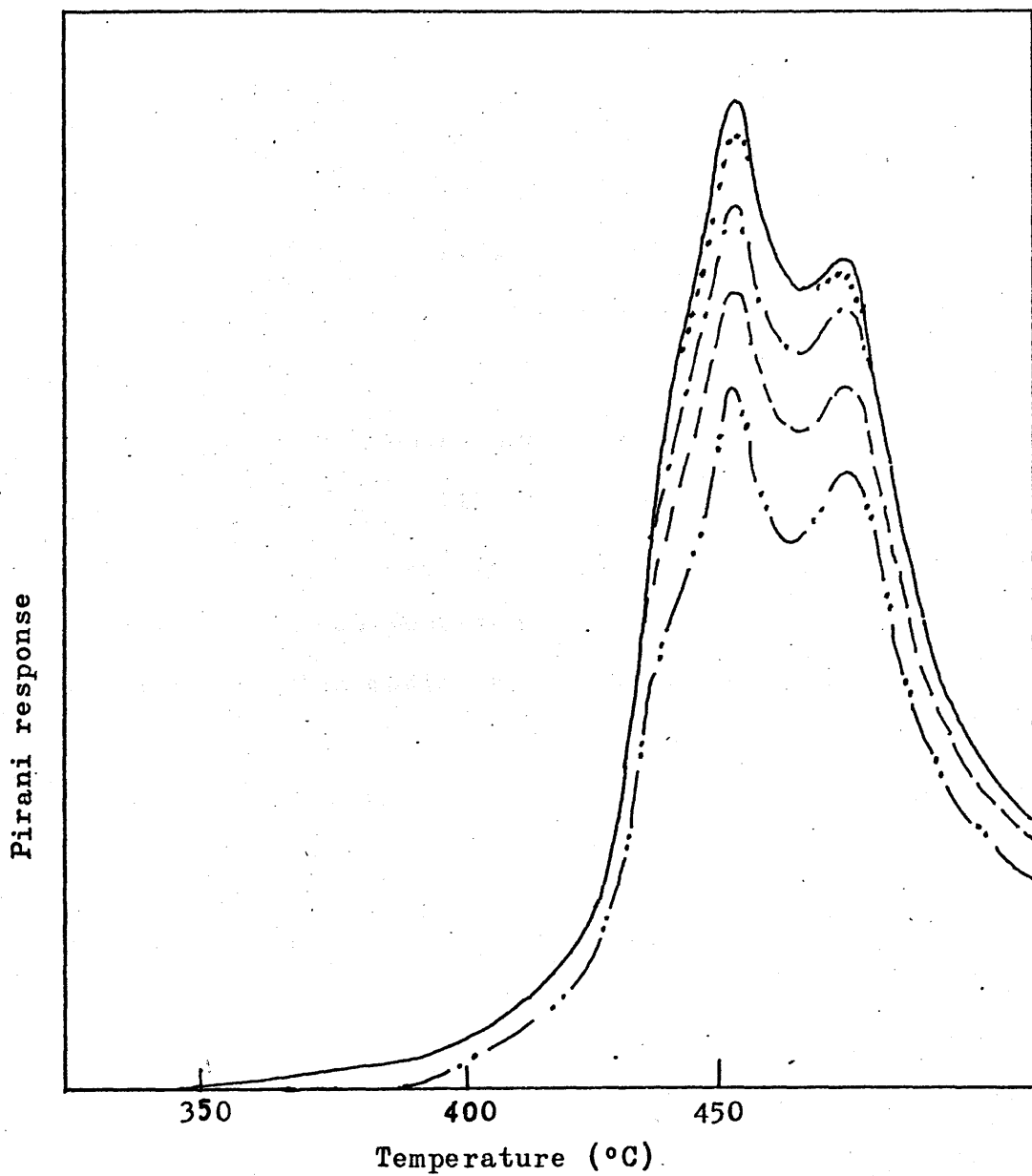
..... -45 where not co-incident with 0° trace

-.- - -75

--- -100 where not co-incident with -75° trace

- - - -196

Fig. 5.3 TVA curve for SrPMA



Trap Temp. °C

— 0

..... -45 where not co-incident with 0° trace

- · - · - -75

---- -100

- - - - -196

Fig. 5.4 TVA curve for BaPMA

are in excess in the case of BaPMA as compared to MgPMA. The presence of carbon dioxide and carbon monoxide may also be due to the decomposition of metal carbonate and interaction of the carbonate with carbon.

T_{base} (the temperature at which the polymer starts degrading) and T_{max} (the temperature at which the rate of evolution is a maximum) are summarised in Table 5.1. The difference in decomposition temperature could be due to the difference in the ionic character of the metal.

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis was carried out under nitrogen and also in vacuum. However, the Du Pont thermobalance cannot be used under vacuum, therefore a Cahn balance was employed for vacuum TGA, using normal TVA conditions. The sample sizes were 5 and 25 mg, when degrading under nitrogen and in vacuo respectively. Figures 5.5, 5.6, 5.7 and 5.8 illustrate weight loss behaviour for the four homopolymers and additional information is given in Table 5.2. The thermogram obtained from the degradation of MgPMA, shows that a slow weight loss starts at a temperature around 250°C and this behaviour persists up to 425°C, above which the rate of weight loss is increased until a plateau appears at 500°C, corresponding to a 31% residue. The early slow weight loss may be due to the decomposition of isotactic segments in the polymer chain, and this has been discussed in the previous section. The plateau at 31% weight loss, in MgPMA, does not correspond to the

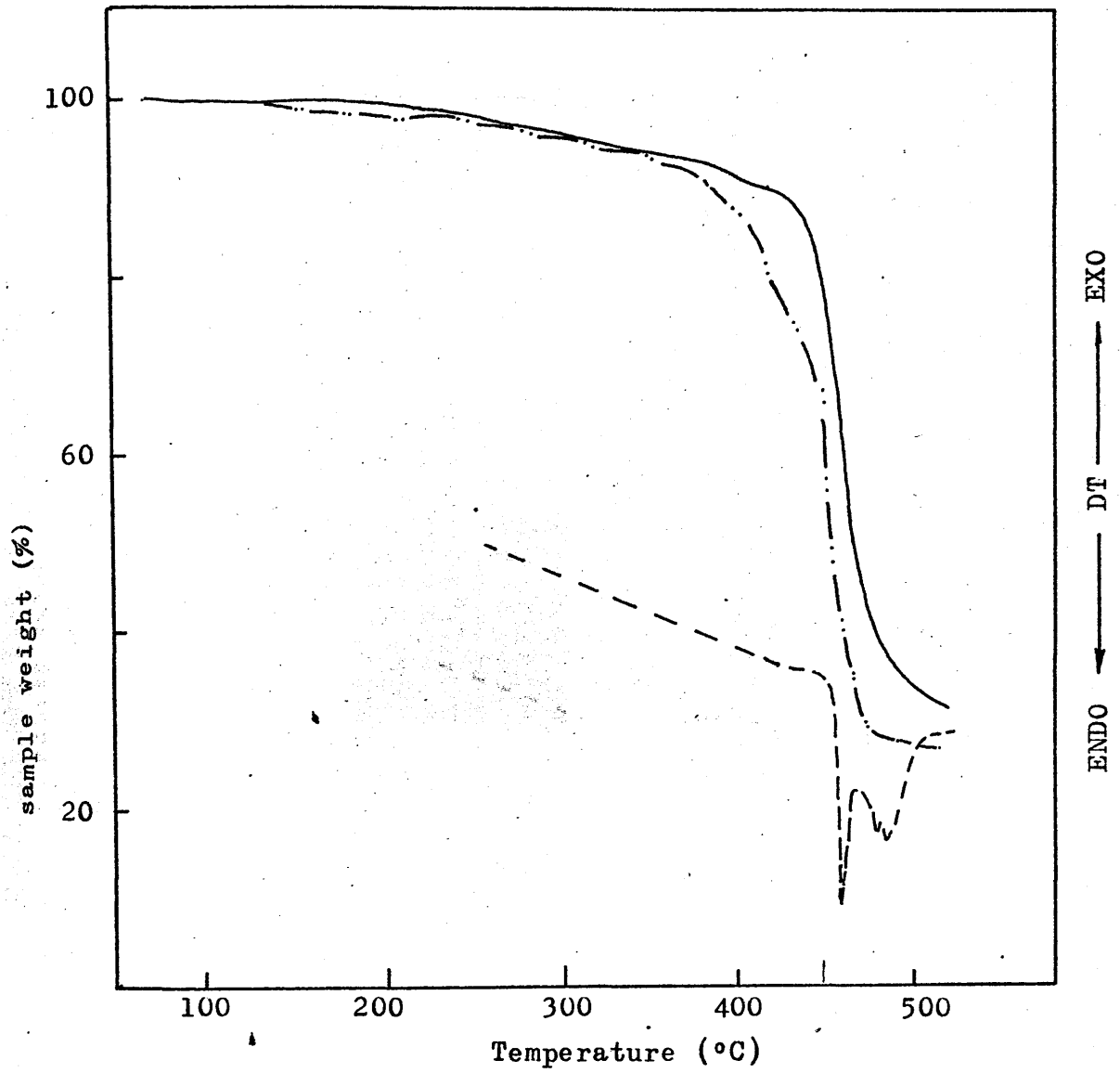


Fig. 5.5 TG and DTA curves for MgPMA

- dynamic N₂ atmosphere
- vacuum
- DTA curve, dynamic N₂ atmosphere

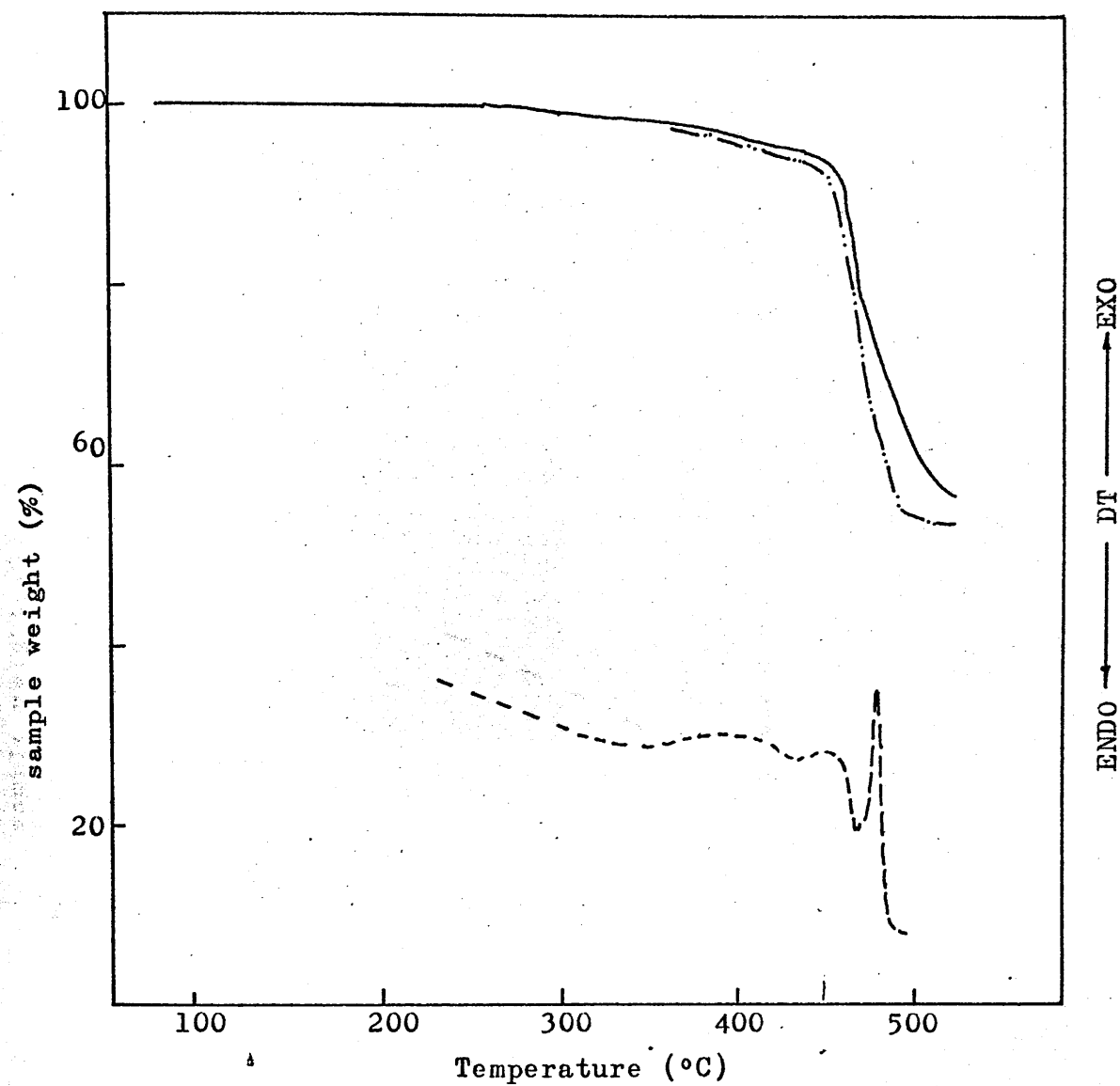


Fig. 5.6 TG and DTA curves for CaPMA

- dynamic N₂ atmosphere
- · - · - vacuum
- - - - DTA curve, dynamic N₂ atmosphere

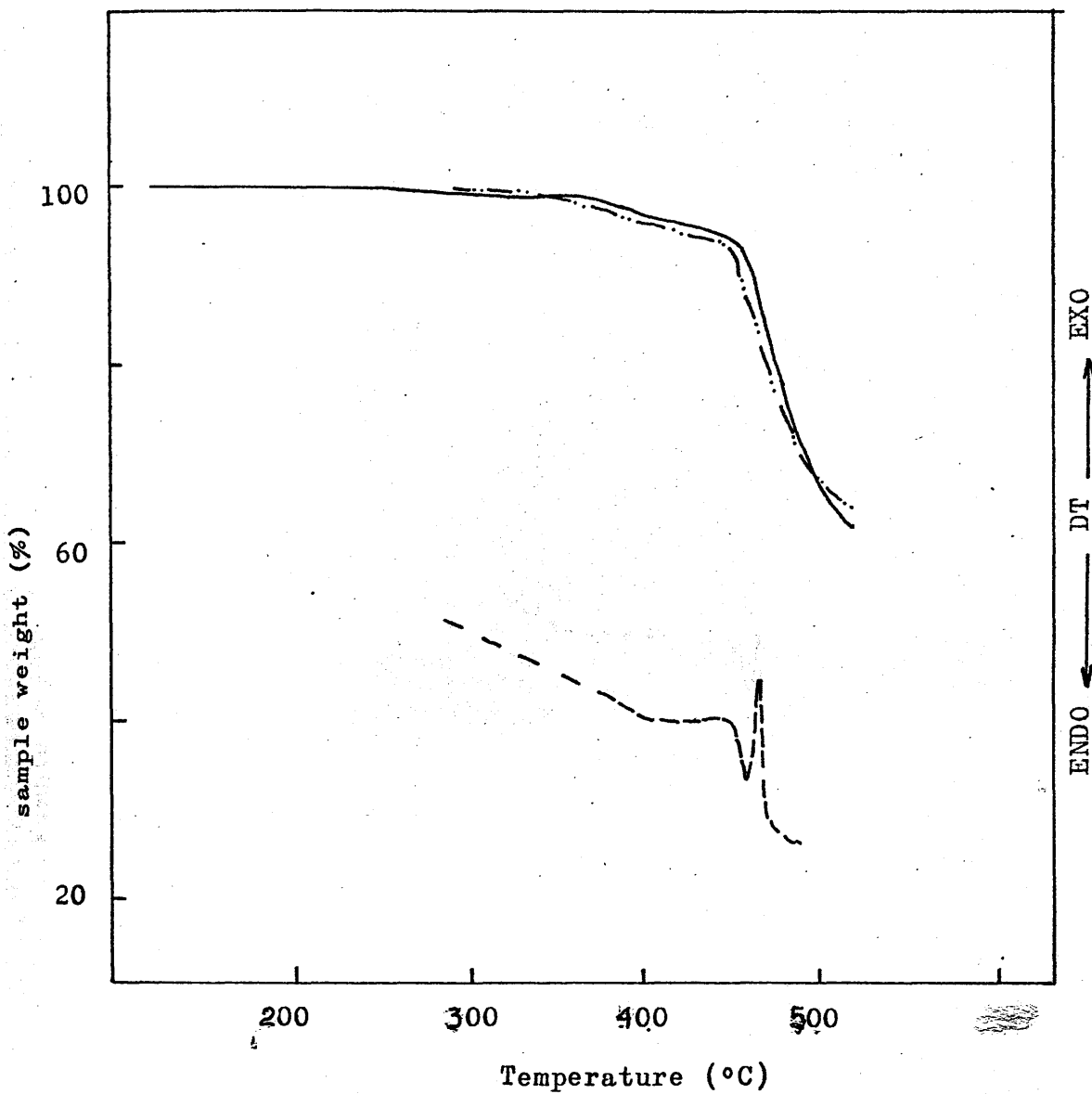


Fig. 5.7 TG and DTA curves for SrPMA

- dynamic N₂ atmosphere
- · - · - vacuum
- DTA curve, dynamic N₂ atmosphere

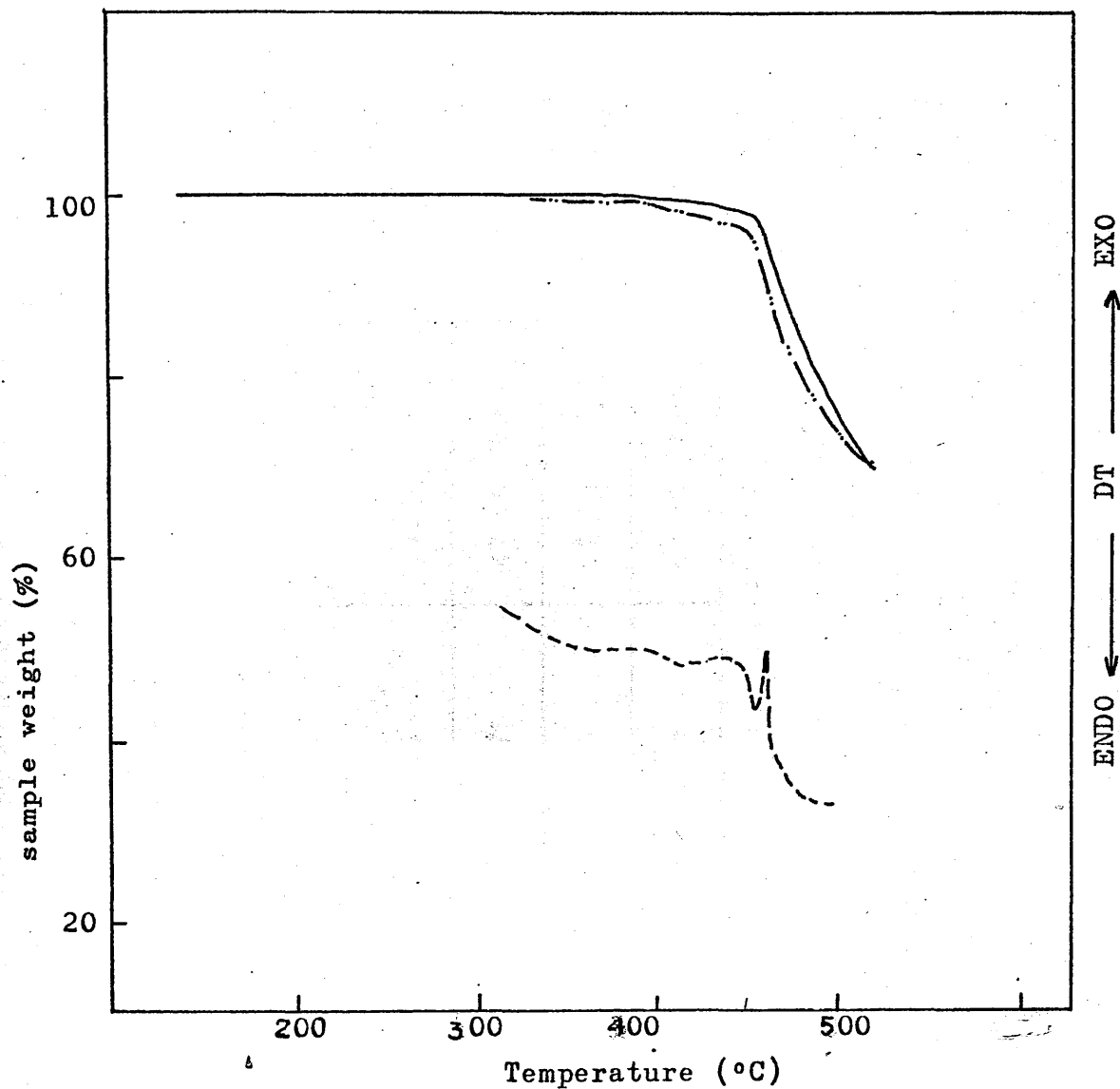


Fig. 5.8 TG and DTA curves for BaPMA

- dynamic N₂ atmosphere
- · - · - vacuum
- DTA curve, dynamic N₂ atmosphere

| Homopolymers | Threshold degradation temperature °C | | Wt. % Residue observed | | Wt. % Residue Calculated |
|--------------|--------------------------------------|--------|------------------------|--------|----------------------------|
| | N ₂ | Vacuum | N ₂ | Vacuum | |
| MgPMA | 260 | 284 | 31.0 | 27.8 | 20.72 (MgO) |
| CaPMA | 350 | 355 | 57.0 | 52.75 | 47.60 (CaCO ₃) |
| SrPMA | 340 | 320 | 61.0 | 63.0 | 57.26 (SrCO ₃) |
| BaPMA | 390 | 386 | 70.0 | 70.0 | 64.17 (BaCO ₃) |

Table 5.2

TG data for MgPMA, CaPMA, SrPMA and BaPMA

Heating rate 10°C/min.

calculated amount of MgO (20.72%). This difference may be attributed to the presence of carbon and undecomposed MgCO_3 . In the case of CaPMA, the plateau at 500°C corresponds to 57% residue which is again 9.4% more than the expected weight of residue as CaCO_3 . This difference decreases in the cases of SrPMA and BaPMA but remains present at 4 to 5%, respectively. It is obvious from TGA curves that polymer samples still show a slow weight loss after 500°C this may be due to some original material not decomposed at that temperature. Analysis of the residues will be discussed in a later part of this chapter to justify the above statement. TGA curves under vacuum show similar behaviour by the polymers.

DIFFERENTIAL THERMAL ANALYSIS

DTA curves for MgPMA, CaPMA, SrPMA and BaPMA are illustrated with TGA traces in Figs. 5.5, 5.6, 5.7 and 5.8 respectively. It is appreciated that the peak maxima in the DTA traces do not represent the true decomposition temperature, but they are adequate for the purpose of comparison. These curves were obtained by using 10 mg samples.

Two endothermic reactions are evident in the four samples, corresponding to an initial and a later fragmentation process. The first broad endotherm may represent the decomposition of isotactic segments in the polymer chain. The second endotherm around 460°C may be attributed to fragmentation of the syndiotactic portion of the chain. It can be seen from DTA traces that the second endotherm around 460°C is followed by an

exotherm around 465°C. This exotherm is probably associated with the cyclization reaction. It is also evident that after the first small endotherm, no exotherm is observed in this temperature region, ruling out possible cyclization. This was further supported by analysis of volatile products obtained from the degradation of polymer heated to 400°C, which showed no cyclic volatile compound. In the case of MgPMA, the second endotherm around 460°C is very sharp and is greater in magnitude than those from the other samples, but instead it gives another broad endotherm around 465°C. This endotherm is again the result of MgCO_3 decomposition which supersedes the exothermic cyclization reaction.

PRODUCT ANALYSIS

The volatile decomposition products were examined after degradation of 100 mg powder sample, in vacuo, to 500°C under the normal conditions of TVA. The liquid products were examined by GLC and noncondensables by IR analysis in a closed system. The condensable volatile gaseous products were also examined by IR analysis.

IR ANALYSIS

IR analysis of the products of homopolymer decomposition established carbon dioxide and dimethyl ketene as the principal gaseous products, together with trace amounts of carbon monoxide, methane, isobutene, butene-1, ethylene, acetylene, benzene and toluene. A typical IR spectrum of the volatile products obtained from the degradation of SrPMA, is shown in Fig. 5.9.

The spectrum is similar to those obtained from alkali metal salts of polymethacrylic acid. The assignments of peaks in the spectrum can be found in Table 4.3. An interesting absorption at 2138 cm^{-1} appears only in the spectrum of divalent salts: $\text{--C}\equiv\text{C--}$ stretch would give rise to an absorption in the region $2140\text{--}2100\text{ cm}^{-1}$. If the structure were $\text{H--C}\equiv\text{C--}$, a peak at 3300 cm^{-1} due C-H stretching would appear. Since this is absent, then if absorption at 2138 cm^{-1} is due to an alkyne, it can only arise from $\text{R--C}\equiv\text{C--R}$. A reference spectrum of $\text{CH}_3\text{--C}\equiv\text{C--CH}_3$ showed absorption at 2135 cm^{-1} , but this was not the strongest absorption, so it is unlikely that the observed absorption is due to an alkyne. Reference spectra of ketene ($\text{CH}_2=\text{C}=\text{O}$) and dimethyl ketene ($\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{C}=\text{O} \\ \diagdown \\ \text{CH}_3 \end{array}$) are included in Fig. 5.9. Both spectra have similar absorptions although the shape is rather different. The reference spectrum of dimethyl ketene has a similar shape to the absorption at 2138 cm^{-1} , therefore it could be assigned to dimethyl ketene. Quantitative measurement of carbon dioxide and dimethyl ketene evolution was obtained by optical density measurement of IR absorptions at 2340 cm^{-1} and 2138 cm^{-1} respectively after collection of the total gaseous products in a 10 cm. path length gas cell. The calibration plots of OD against pressure as given in Chapter 2 were used to obtain the mole % of carbon dioxide and dimethyl ketene, per monomer unit, summarised in Table 5.3. The formation of dimethyl ketene will be discussed along with the mechanism resulting in formation of other ketones in the

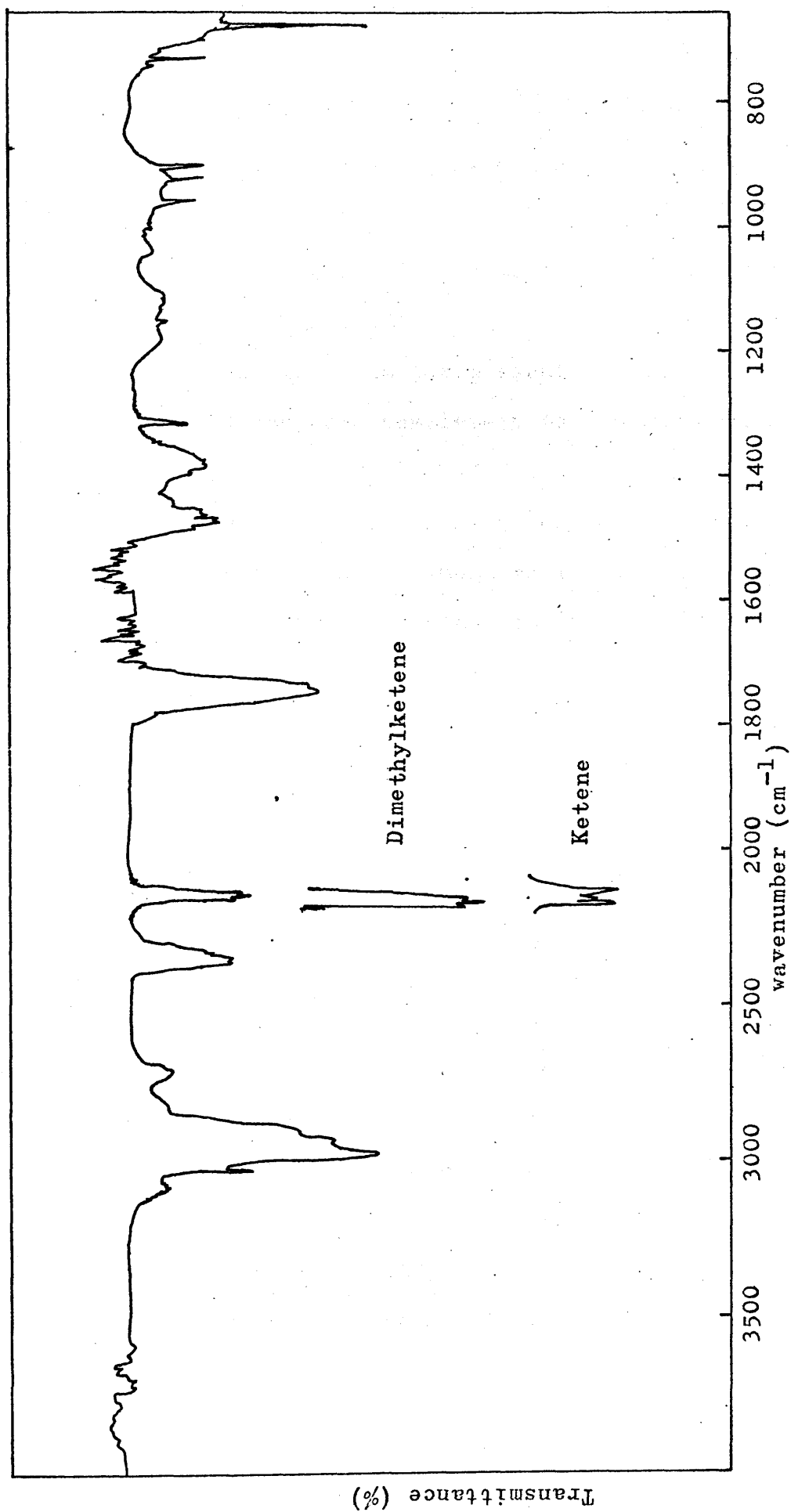


Fig. 5.9 IR spectrum of gaseous volatile products from SrPMA degraded to 500°C

degradation of homopolymers but carbon dioxide evolution is discussed below.

It seemed that carbon dioxide is a straightforward result of the decomposition of metal carbonates as these are formed in homopolymer degradation. In the present studies, it was found that pure MgCO_3 decomposed completely to MgO and carbon dioxide at 500°C , whereas only a fraction of a CaCO_3 sample was decomposed at this temperature. The other metal carbonates were stable at 500°C but SrPMA and BaPMA gave measurable amounts of carbon dioxide. The only possible explanation to this contradiction which could be given, is that during degradation the other products, such as ketones and carbon, may act as impurities to the metal carbonates produced and lower their decomposition temperature.

The systematic decrease in the evolution of carbon dioxide from the homopolymers, can be explained on the basis of the remarks made by Cotton and Wilkinson.

Calcium, strontium, barium and radium form a closely allied series in which the chemical and physical properties of the elements and their compounds vary systematically with increasing size. The ionic character and electropositive nature is greatest for Ra . and the thermal stability of the carbonates increases with the size of the ion. In present studies, a graph plotted between ionic radius and the carbon dioxide produced from the degradation of CaPMA , SrPMA and BaPMA gave a linear relationship, but it lost its linearity after including carbon dioxide from NgPMA . This deviation is quite consistent with the well known

| Homopolymer | * Charge ionic radii | mole % of CO ₂ per monomer ² unit | mole % of dimethyl ketene per monomer unit |
|-------------|----------------------------|---|--|
| MgPMA | 3.3 Mg ²⁺ | 4.90 | 0.07 |
| CaPMA | 1.8 Ca ²⁺ | 2.95 | 0.11 |
| SrPMA | 1.2 Sr ²⁺ | 1.90 | 0.13 |
| BaPMA | 1.0 Ba ²⁺ | 1.55 | 0.13 |

* Reproduced from ref. 67.

Table 5.3

Quantitative evolution of carbon dioxide and dimethyl ketene
per monomer unit.

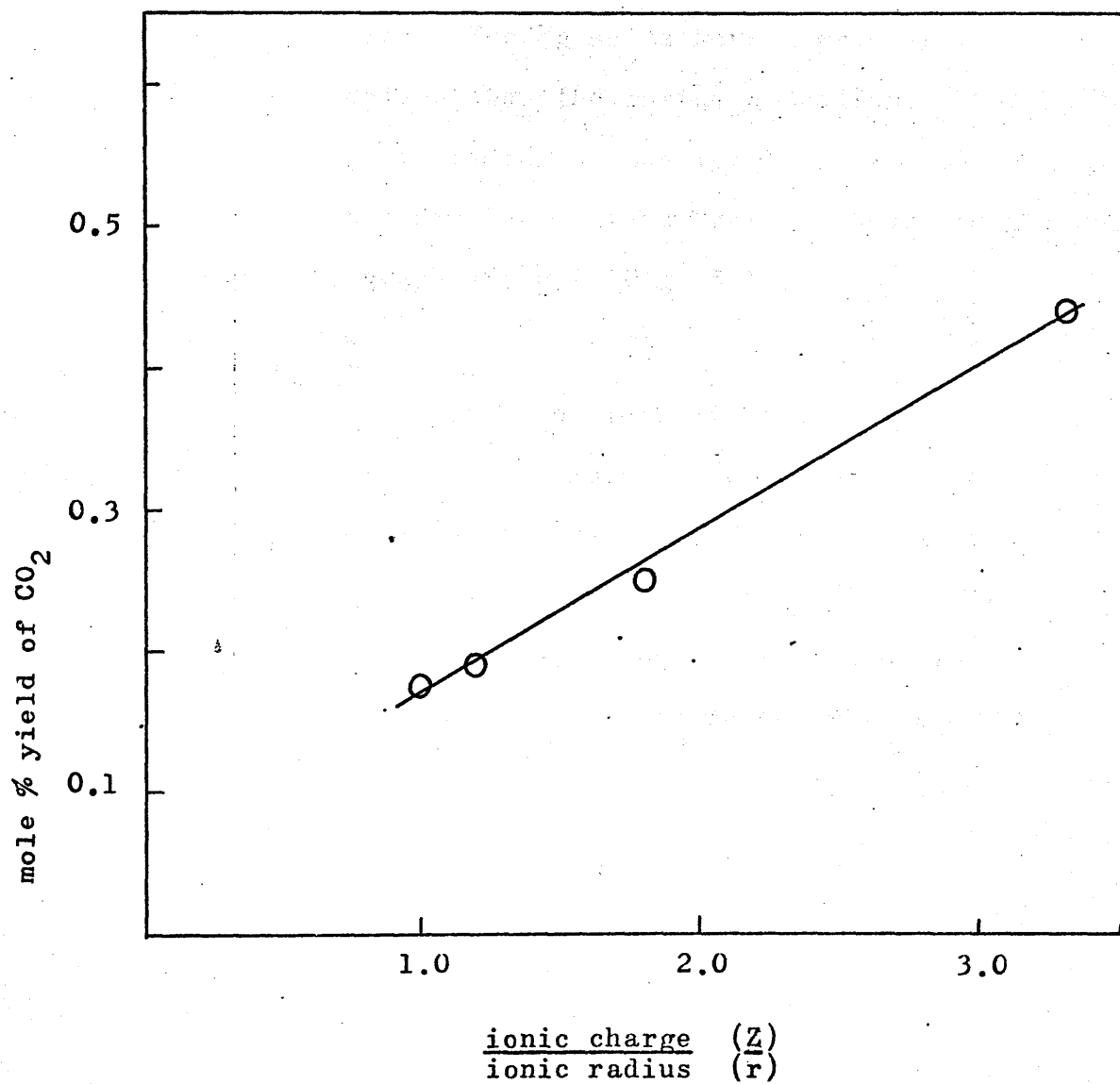


Fig. 5.10 Evolution of carbon dioxide versus ionic charge/ionic radius

property of Mg that it does not show a close relationship with the heavier members. The increasing ionic character and thermal stability of metal carbonates suggests that the lattice energy and ionic nature of metal carbonate lattices increase with the size of the metal ion. The Mg salts have a greater tendency to covalent bond formation than the barium or radium. Thus if the ratio of the charge to radius of the metal is plotted against the amount of carbon dioxide evolved from the four homopolymers, this leads to the graph shown in Fig. 5.10.

GAS CHROMATOGRAPHY

IR analysis does not allow identification of all the liquid products, particularly the various ketones. GLC was employed for qualitative and quantitative analysis of the liquid products and the measurements were carried out on a Perkin-Elmer F11 Gas Chromatograph at 60°C, using a column containing 13½% MEA and 6½% Di-2-ethyl Hexyl Sebacate on chromosorb, with N-butanol as internal standard. The sensitivities of the products compared to the standard were measured, using the method of cut-outs to determine peak area as noted in Chapter 2. Analysis was made of products obtained by degrading 100 mg powder samples to 500°C at 10°C/min, under vacuum.

A typical chromatogram for the products from CaPMA is shown in Fig. 5.11. The early peaks A and B, are of air and ether respectively. Ether is retained by the syringe after cleaning. Peak C is assigned to chloroform which is an impurity from the apparatus, which is usually cleaned with this solvent. The

Table 5.4

Quantitative yield of liquid volatiles
per monomer unit.

| Peak No. | Liquid Volatile | mole % of liquid volatile per monomer unit | | | |
|----------|--|--|-------|-------|-------|
| | | MgPMA | CaPMA | SrPMA | BaPMA |
| 1 | CH_3CHO | trace | trace | trace | trace |
| 2 | $\text{CH}_3\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{.CH}_3$ | " | " | " | " |
| 3 | $\text{CH}_3\text{CH}_2\text{.CHO}$ | " | " | " | " |
| 4 | $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \text{.CHO} \\ \diagup \\ \text{CH}_3 \end{array}$ | 0.49 | 1.71 | 2.09 | 1.36 |
| 5 | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CHO} \end{array}$ | trace | trace | 0.55 | 2.06 |
| 6 | $\text{CH}_3\text{CH}_2\text{CH}_2\text{.CHO}$ | " | " | 1.10 | 1.32 |
| 7 | H_2O | " | " | trace | trace |
| 8 | $\text{CH}_3\text{CH}_2\text{COCH}_3$ | 1.23 | 1.63 | 1.84 | 1.73 |
| 9 | C_6H_6 (Benzene) | trace | trace | trace | trace |
| 10 | $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \text{.CO.CH}_3 \\ \diagup \\ \text{CH}_3 \end{array}$ | 0.50 | 1.55 | 1.40 | 1.10 |
| 11 | $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CO.CH}_3 \\ \\ \text{CH}_3 \end{array}$ | trace | trace | 0.46 | 0.51 |
| 12 | $\text{CH}_3\text{CH}_2\text{.}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{.CH}_2\text{.CH}_3$ | 2.76 | 3.47 | 2.40 | 1.97 |
| 13 | ? | trace | trace | trace | trace |

Table 5.4 (Continued)

Quantitative yield of liquid volatiles
per monomer unit

| Peak No. | Liquid Volatile | mole % of liquid volatile per monomer unit | | | |
|----------|---|--|-------|-------|-------|
| | | MgPMA | CaPMA | SrOMA | BaPMA |
| 14 | $\text{CH}_3-\text{CH}=\text{CH}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$ | 2.54 | 6.78 | 3.85 | 1.76 |
| 15 | $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CO}$ | 0.43 | 0.98 | 0.55 | trace |
| 16 | | trace | trace | trace | trace |
| 17 | | " | " | " | " |
| 18 | $\text{CH}_3\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ | internal standard | | | |
| 19 | Mesityloxide | trace | trace | trace | trace |
| 20 | | 0.29 | " | 0.67 | 0.47 |
| 21 | | trace | " | trace | trace |
| 22 | | 0.40 | 0.86 | 1.28 | 0.86 |
| 23 | | trace | trace | trace | trace |
| 24 | | 0.73 | 1.38 | 1.43 | 1.06 |
| 25 | | 2.68 | 2.81 | 2.14 | 1.44 |

12.05 21.37 19.76 15.64

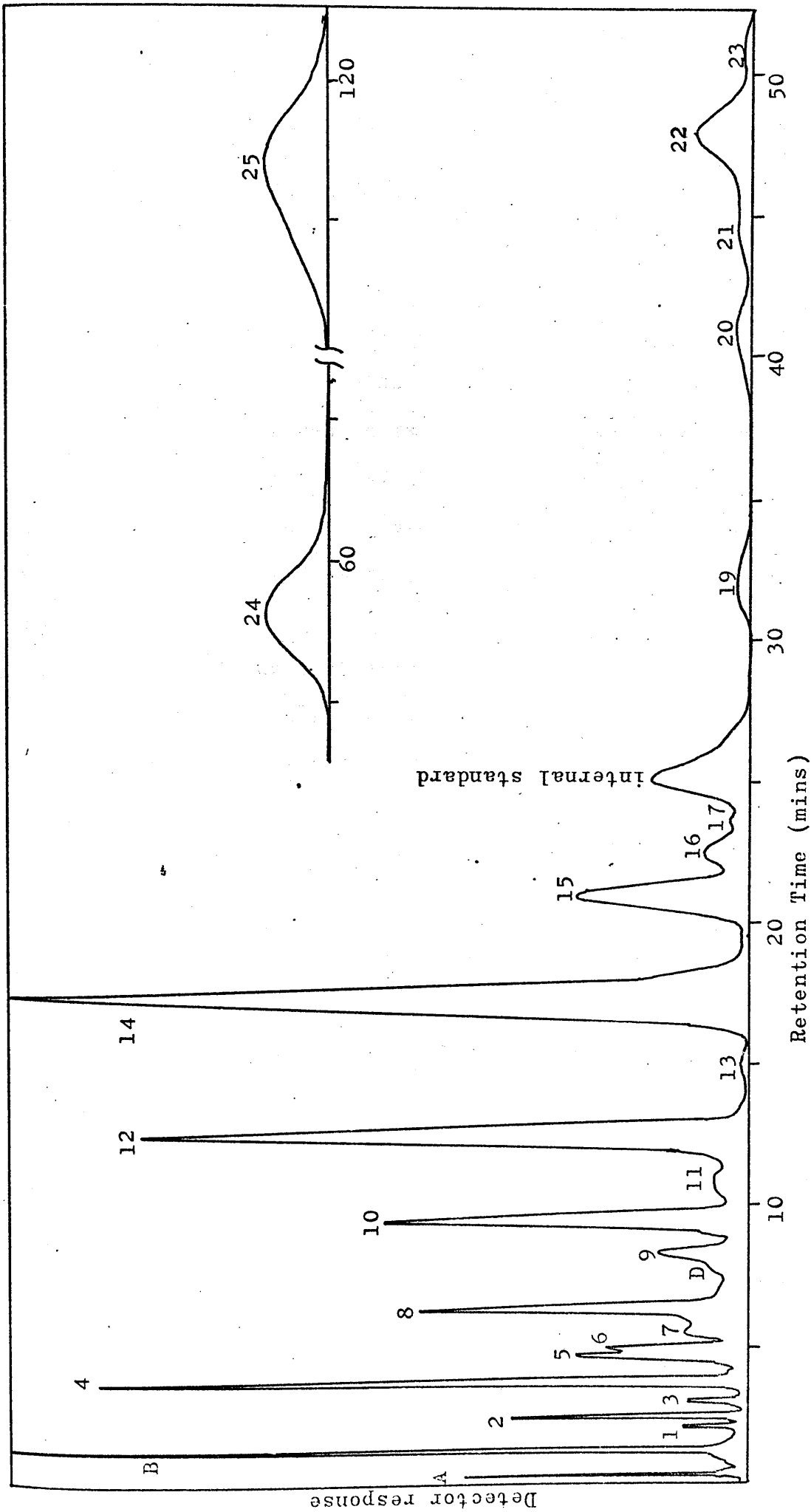


Fig. 5.11 GLC trace of liquid degradation products from CaPMA, Column temperature 60°C;

Helium Carrier gas, 35 ml/min.

identification of the peaks was carried out by comparing the retention times of the known compounds. Altogether, there are 24 peaks in the chromatogram and reproducibility of these was obtained, employing a column containing 10% PEG400 at 70°C.

The quantitative yields in mole % of liquid volatile products are summarised in Table 5.4. It appears from the amounts obtained that no simple correlation exists between the four homopolymers and the volatile products obtained. A number of principle features, however, may be summarised as follows:-

- a. The total amounts of aldehydes produced increase as the size of metal ion increases (Mg→Ba).
- b. The yields of aliphatic ketones such as methylethyl, diethyl, di-isopropyl methyl-n-propenyl and methyl isopropyl ketone decrease from calcium to barium.
- c. The amount of 2,5-dimethyl cyclopentenone liberated from calcium, strontium and barium polymethacrylate, decreases as the size of the ion increases. This may be the net result of cross-linking which can occur in the case of polymers containing larger cations, resulting in steric hindrance.
- d. The total amounts of cyclic ketones cannot be correlated with the size of the metal ion in the four homopolymers, since MgPMA, CaPMA, SrPMA and BaPMA give 4.1, 5.0, 5.5 and 3.8 mole % of cyclic ketone respectively. Thus the role of the metal in the degradation of these homopolymers is not clear, but it seems that factors other than metal ion size are also involved, such as the presence of crosslinked units and isotactic segments.

Crosslinked units are more likely to produce aliphatic ketones or hydrocarbons than cyclic ketones. It was noted earlier that in the TVA curves the size of the first peak decreases as the size of the metal ion increases; it was argued that this decrease in area was a result of a decrease in the number of isotactic units in the chain. The products obtained from the first peak were aliphatic ketones, CO_2 and hydrocarbons, rather than cyclic ketones.

e. The total amounts of liquid products decrease from calcium to barium polymethacrylate but MgPMA produces the lowest amount of liquid volatiles. This is because MgPMA produces a larger cold ring fraction than the other three polymers. The cold-ring fraction of MgPMA consists of chain fragments which have a similar structure to that of the polymer. The other three homopolymers do not produce a cold-ring consisting of chain fragments, perhaps because the metal part of these is too heavy to volatilize. The structural detail and quantitative yields of these will be given in the following section.

COLD-RING FRACTIONS

IR spectra of the CRF's obtained on degradation of the four homopolymers did not provide the best insight into the structural rearrangements which can take place. Calcium, strontium and barium polymethacrylate produced similar types of CRF at 500°C . The yellow CRF spectra were obtained using the KBr disc technique. The main peaks observed were:

| MgPMA | CaPMA | SrPMA | BaPMA |
|--------------|-------|--------|-------|
| wt. % of CRF | | | |
| 22.2% | 6.12% | 10.26% | 5.4% |

Table 5.5

Weight % of CRF from MgPMA, CaPMA,
SrPMA and BaPMA.

| | |
|-----------------------------|---|
| 2845, 2920 cm^{-1} | C-H stretching |
| 1680-1700 cm^{-1} | C=O stretching |
| 1600-1610 cm^{-1} | -C=C- or ring structure |
| 1450 cm^{-1} | C=O stretching or alkanes |
| 1375 cm^{-1} | -CH ₂ -CH ₂ - alkanes |
| 815 cm^{-1} | Olefinic C-H |
| 880 cm^{-1} | Olefinic C-H |

These peaks cannot be assigned to a particular compound but lead to the assumption that the CRF is a mixture of hydrocarbons and chain containing ketonic group. These may arise from the unsaturated hydrocarbons and ketones containing double bonds.

Degradation of MgPMA to 500°C gave two types of cold-ring fraction, one yellow similar to those above and the other a pale brown powder which had a spectrum similar to those of the original polymer and magnesium isobutyrate. This arises from the sublimation of these compounds at that temperature. The weight %'s of cold-ring obtained from the homopolymers are summarised in Table 5.5 to supplement the above information.

RESIDUE ANALYSIS

100 mg powder samples of the homopolymers were degraded to 500°C at the rate of 10°C/min, under the normal conditions of TVA, and the black residue left at the base of the degradation tube was studied by IR analysis using the KBr disc technique. The main peaks found in the spectra were:-

I MgPMA

2960, 2920, 2860, 1550,
1410, 410-580(s.b.) cm^{-1}

II CaPMA

2510, 1790, 1450(s), 878,
715, 535, 310(s) cm^{-1}

III SrPMA

2975, 2870, 2500, 1780,
1550(W), 1450(s.b.), 875, 710, 270-240(s.b.) cm^{-1}

IV BaPMA

2975(W), 2870(W), 2480(W), 1760(W),
1550(W), 1420-1400(s.b.), 1070(W), 870(S),
700, 690(W), and 220-260(b) cm^{-1}

The peaks at 2960 to 2860 and 1550 cm^{-1} , present in the cases of MgPMA, SrPMA and BaPMA, correspond to undegraded residual polymer sample. These bands are absent in the spectrum of CaPMA, indicating complete degradation of this sample. The band intensities of residual samples of MgPMA, SrPMA and BaPMA suggest that a significant amount of undegraded polymer is left in the case of MgPMA and only traces left from SrPMA and BaPMA. MgPMA gave a residue consisting of MgO and carbon rather than the undegraded polymer. There was no trace of MgCO_3 detected in the spectrum. In the cases of Ca, Sr and BaPMA, the bands observed in the region of 1400, 900 and 500 to 200 cm^{-1} correspond exactly to those of their respective carbonates and

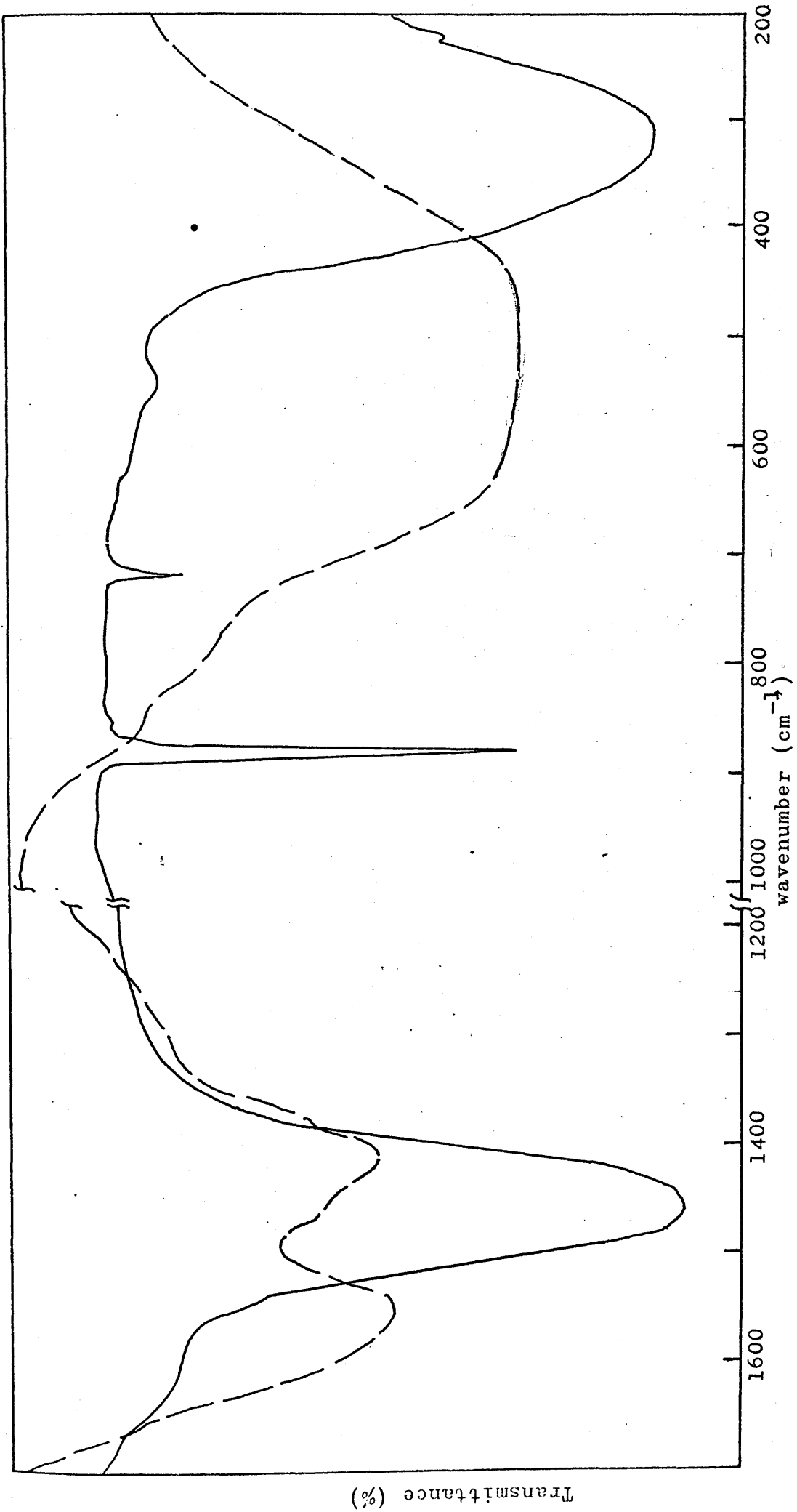


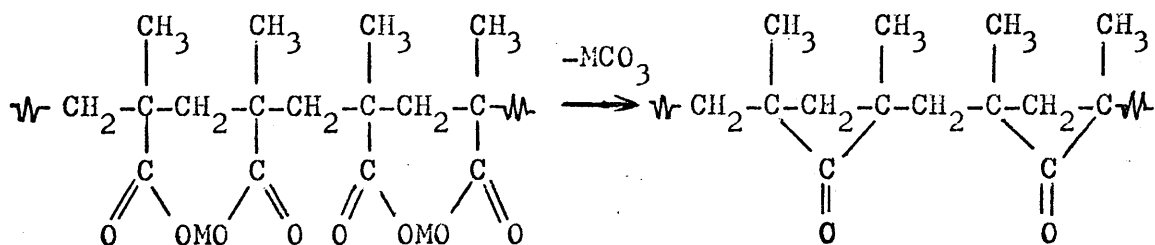
Fig. 5.12 IR spectra of residues from: — CaPMA and ---MgPMA

oxides. Typical spectra of residues left after degradation to 500°C are shown in Fig. 5.12.

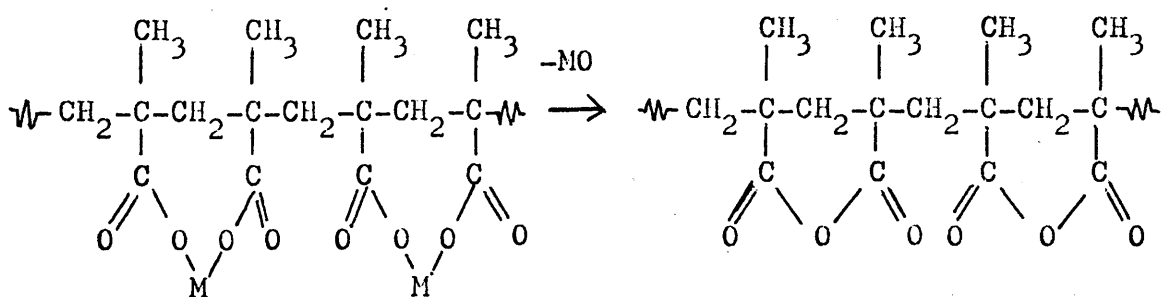
STRUCTURAL CHANGES DURING DEGRADATION

The production of aliphatic and cyclic ketones, metal carbonate and metal oxide, are indicative that the following course of degradation may occur.

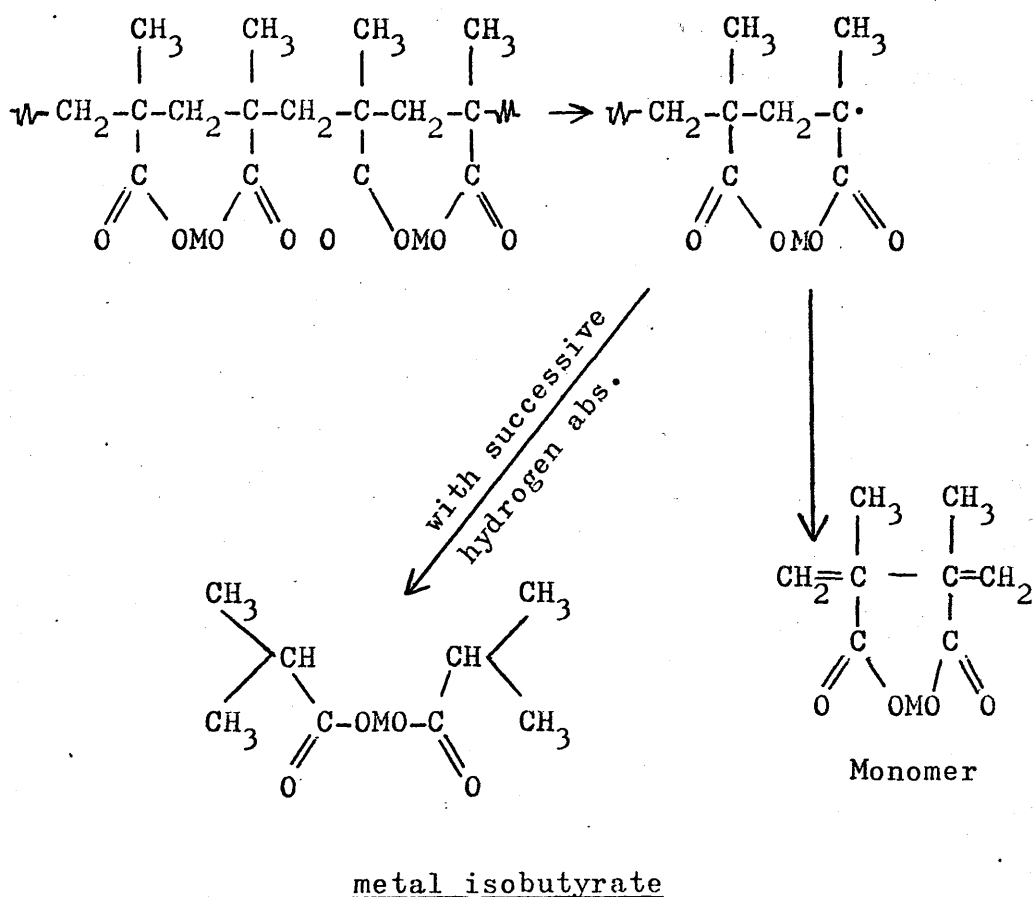
a. Intramolecular formation of MCO_3 which can result in the polymer chain containing four membered cyclic rings.



b. Intra or intermolecular formation of metal oxide (MO), which can yield anhydride structures.



c. Depolymerization to monomer, or a similar compound such as isobutyrate, with successive hydrogen abstraction.



In order to investigate the above structural rearrangements postulated on the basis of products formed, 100 mg of the polymer sample was heated at 400°C both by programmed and isothermal heating. All four homopolymers seemed to follow a similar course of degradation, and therefore a detailed account of only MgPMA is given in this section.

Fig. 5.12 illustrates the IR region of primary interest, in (a) MgPMA, (b) MgPMA heated to 390°C at 10°C/min (the first peak max), (c) MgPMA heated to 440°C at 10°C/min (the second peak max), (d) magnesium isobutyrate. Fig. 5.12(b) shows the original band of MgPMA to occur with weaker intensity and indicates the appearance of new absorptions at 1300, 1100, 930

and 840 cm^{-1} . These new bands correspond to the spectrum of magnesium isobutyrate as shown in Fig. 5.12(d). The disappearance of the original bands of MgPMA and the formation of magnesium isobutyrate become more evident after the polymer is heated to the second peak maximum of the TVA curve at 440°C as in Fig. 5.12(c). Figs. 5.12(b) and (c) are also indicative of a broad absorption at 400 cm^{-1} , which is characteristic of MgO. The absence of sharp bands around 860 and 700 cm^{-1} is indicative of the absence of MgCO_3 , which may, therefore, be decomposing as it is formed. It does not seem that MgO was forming as a primary product in the decomposition of polymer, because if this were the case then the IR spectra of the residues should have shown absorptions around 1800 and 1020 cm^{-1} , characteristic of anhydride structures. The initial formation of MgCO_3 rather than MgO could result in the residual four membered cyclic ketonic structures as in (a), but on the other hand, the energy consideration and the high temperatures involved would make it impossible to observe such intermediate structures in the residue. Thus the absence of absorption at 1750 cm^{-1} (C=O stretching), a characteristic band for cyclic ketonic structure, leads to the assumption that four membered cyclic rings leave the chain as soon as they are formed.

Another interesting weak absorption at 1240 cm^{-1} in Fig. 5.12(c) can be assigned to monomer as noted in Chapter 3.

Molecular weight changes were not followed during temperature-programmed degradation of the homopolymers but it was possible to obtain similar information by heating 100 mg

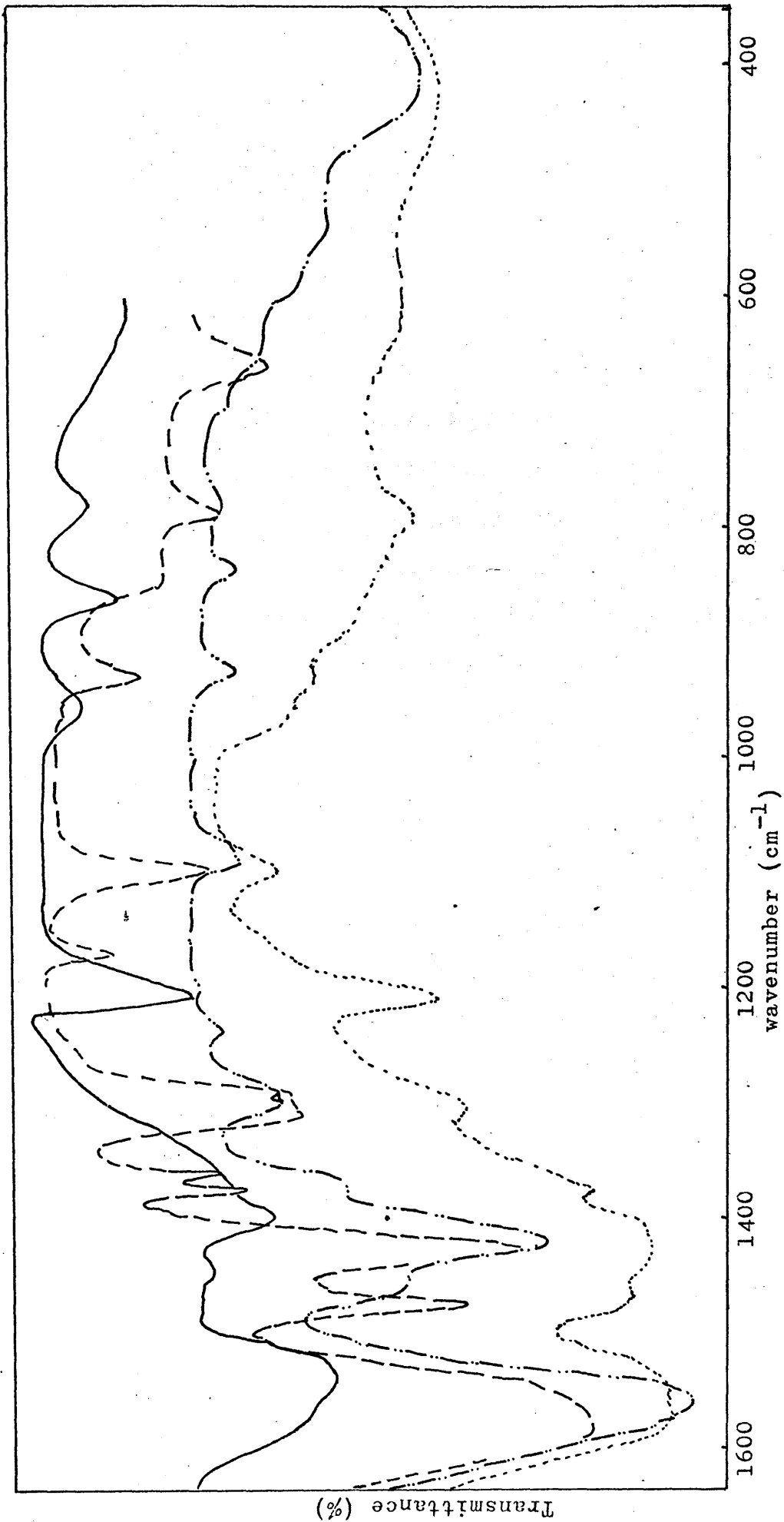


Fig. 5.13 Infra-red absorption spectra of: (a) — MgPMA, (b) MgPMA heated to 390°C, (c) - - - - - MgPMA heated to 440°C (d) - - - - - magnesium isobutyrate.

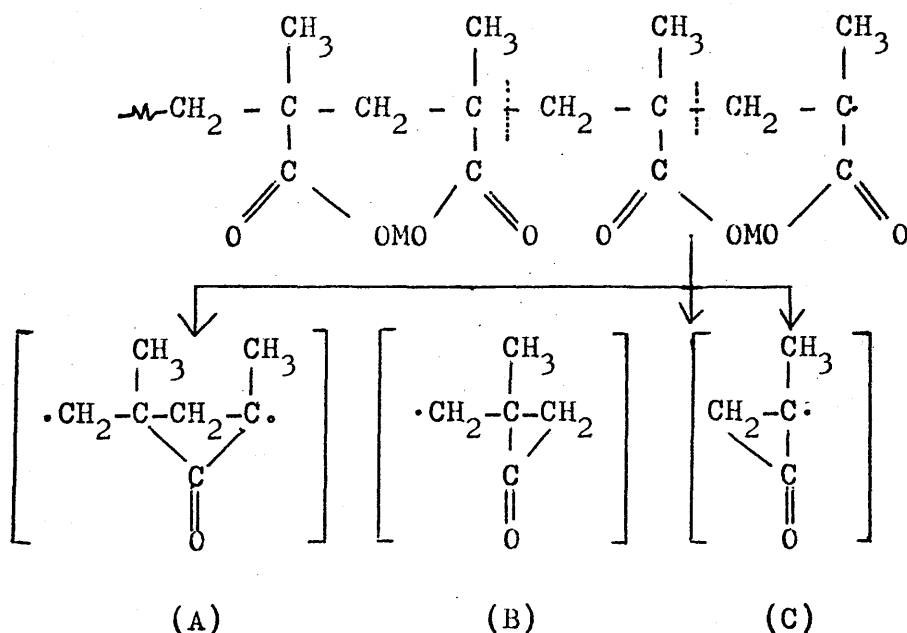
samples at 400°C for 30 min. and one hour isothermally. The residue at these temperatures was stirred into 25 ml of distilled water and filtered. The filtrate was evaporated at room temperature in a rotary evaporator and IR spectra showed the samples to consist of MgPMA, MgMA and magnesium isobutyrate. The soluble MgPMA must be of low molecular weight compared to the original sample because originally the homopolymer was found to be completely insoluble in water. The black insoluble portion gave a spectrum of MgPMA and MgO. The production of monomer and low molecular weight polymer is indicative of a reaction parallel to the depolymerisation of poly (methyl methacrylate).

DISCUSSION

There seems to be a marked similarity in the thermal breakdown of monovalent and divalent salts of polymethacrylic acid. The difference is in the relative amounts of liquid volatile products and it may be attributed to the difference in the nature of the monovalent and divalent metals.

Two distinct processes may be discerned during the thermal-decomposition of salts of PMAA, namely, (a) carbonate formation by intramolecular reaction resulting in the elimination of four membered cyclic ring structures followed by their successive modification to cyclic or aliphatic ketones, (b) chain scission leading to the formation of monomer or metal isobutyrate irrespective of whether carbonate formation or chain scission takes place first, the essence of the proposed

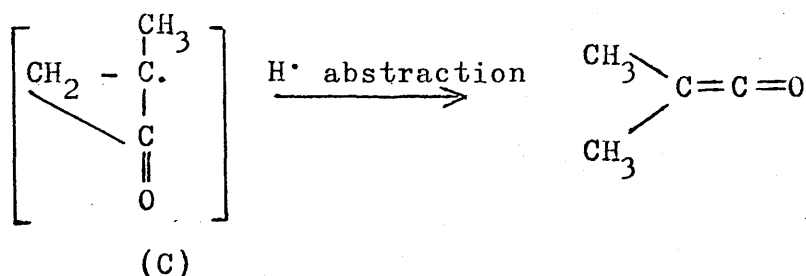
mechanism is that carbonate formation leaves three types of radical species.



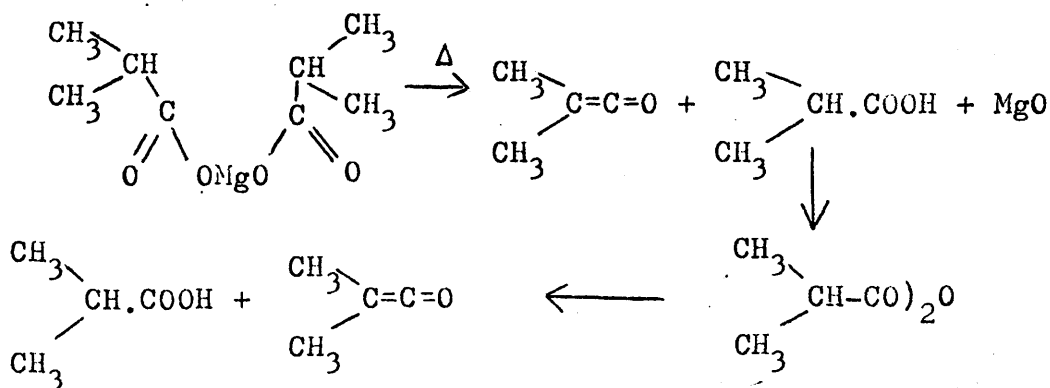
The formation of liquid products can occur by the change of the ring structures as illustrated in Chapter 4. The intermediate (A) can give cyclopentanone rings or ring cleavage can occur with loss of methane to give diethyl ketone. The species (B) can give methyl isopropyl ketone, methy-n-propenyl ketone, methyl isopropenyl ketone and with prior loss of a methyl group, it can also give methyl ethyl ketone. The intermediate species (C) can give isobutyraldehyde, n-butyraldehyde, methacrolein and with the loss of methane prior to product formation, it can give propionaldehyde and acetone.

Dimethyl ketene is the only product peculiar to the divalent metal salts of polymethacrylic acid. This product was not detected in the degradation of monovalent salts of

polymethacrylic acid. One could simply argue that it can be formed from the intermediate species (C) as there is extensive hydrogen transfer taking place during the reaction.



But this does not seem to be valid because if the species (C) were responsible for the formation of dimethyl ketene, then monovalent salts should produce a sufficient amount to enable detection, as such an intermediate is also postulated in the case of monovalent salts. On the other hand it seems that dimethyl ketene may be formed from metal isobutyrate. It has been noted in Chapter 3 that magnesium isobutyrate decomposed to dimethyl ketene under the normal conditions of TVA at 500°C. The monovalent salts of isobutyric acid do not give any ketene, possibly because they sublime under the TVA conditions. The mechanism for the formation of dimethyl ketene could simply be written in the following way.



The formation of the ketene from isobutyric anhydride by the above route has been postulated by Pregaglia.¹⁰⁶

On the basis of the above mechanism, one might expect some isobutyric acid in the products but it was not identified by GLC or IR in the present studies.

C H A P T E R S I X

THERMAL DEGRADATION OF ZINC POLYMETHACRYLATE

INTRODUCTION

The thermal degradation of monovalent and divalent salts of polymethacrylic acid has been described in Chapters 4 and 5. These studies showed that a complex series of reactions occur at the decomposition temperature, but prominent features are depolymerization and interaction of the pendant carboxylate groups. Zinc polymethacrylate exhibits a similar pattern of degradation but yields different amounts of volatile products than do other divalent metal salts, and because of this lack of correlation, the thermal degradation of ZnPMA is described separately in this Chapter.

EXPERIMENTAL

Polymer preparation, purification and characterization has been described in Chapter 2.

Results and Discussion

All the sample sizes mentioned in the forthcoming discussion refer to a pure sample, excluding moisture and precipitant as determined by thermogravimetry.

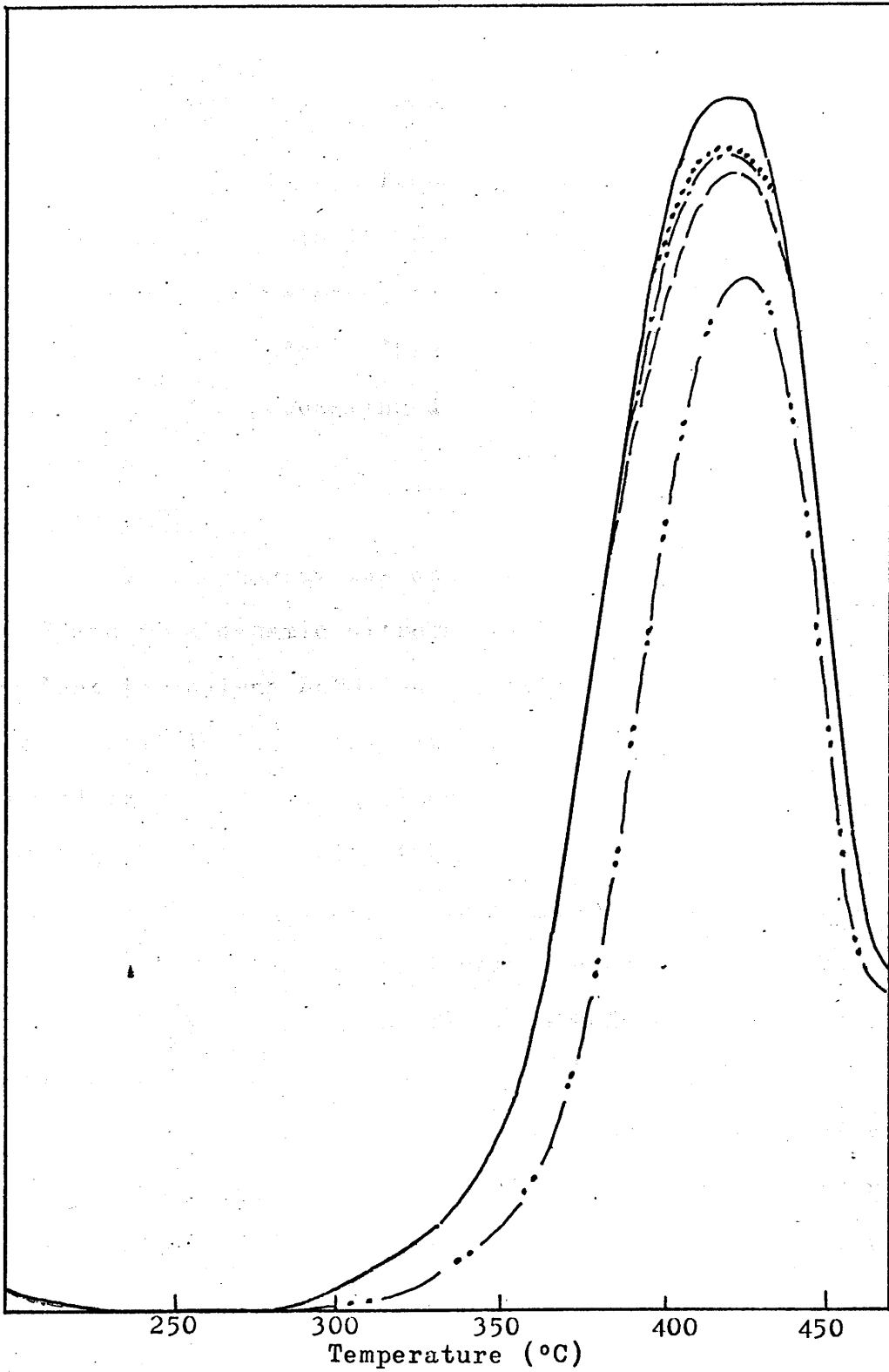
Thermal Volatilization Analysis

Figure 6.1 illustrates the TVA curves for a 50 mg powder sample of ZnPMA. The same diagram also incorporates the key to the traces for the different trap temperatures used.

The polymer sample was heated to 500°C at a rate of 10°C/min under the normal conditions of TVA. The trace reveals a slow release of volatile material at 60°C and this evolution is complete at 250°C. IR analysis of the volatile product in this region showed only methanol and traces of water, which are retained by the polymer during purification. At 297°C, a further slow release of volatile products begins which becomes gradually more rapid, resulting in a rate maximum at 424°C (T_{\max}).

It is obvious from Fig. 6.1 that from the early stage of this peak to the T_{\max} , the -196° and 0°C curves are well separated from each other. This indicates that degradation results in products condensing at -196° together with non-condensable products which pass through this trap. A further interpretation of the TVA curve indicates the presence of high boiling products, since the 0° and -45° traces are well apart from each other. This separation could result only if volatile products pass through the 0° trap but condense in the -45° trap. These products are likely to be ketones. The overlap of the -45° and -75° traces and their separation from the -100° trace could be due to the presence of low-boiling ketones, aldehydes and carbon dioxide. In fact these types of products were identified, as will be shown in the latter part of this Chapter. Fig. 6.1 also indicates that after the T_{\max} (424°C), the separation of the 0, -45, -75, -100 and -196°C traces begins to decrease and ultimately they all come

Pirani response



Trap Temp. °C

— 0

..... -45 where not co-incident with 0° trace

- · - · -75 where not co-incident with 0 and -45° traces

--- -100 where not co-incident with 0, -45 and
-75° traces.

- - - -196

Fig. 6.1 TVA curve for ZnPMA

to coincidence. It was found that at this stage of degradation the volatile products comprised mainly of carbon monoxide, methane, carbon dioxide and traces of ketones and aldehydes. This could be the result of the decomposition of crosslinked polymer and the reduction of ZnO by carbon.

Thermogravimetry

A TGA thermogram was obtained using a heating rate of $10^\circ\text{C}/\text{min}$ in a dynamic nitrogen atmosphere. It is not convenient to analyse ZnPMA on the Cahn balance used for the other metal salts because zinc metal, produced as a degradation product, sublimes and is deposited on the wires holding the pan. This metal deposit causes interference with the normal operation of the Cahn balance. The amount of residue left at 500°C , under normal conditions of TVA, was determined by weighing the TVA tube before and after degradation.

Fig. 6.2 illustrates the result for a 10 mg powder sample and exhibits a one-stage weight loss in the same temperature region as the evolution of volatile products observed in TVA experiments. The initial weight loss below 200°C is due to the release of moisture and precipitant retained by the polymer sample, while formation of volatile products and other chain fragments comprises 49.4% of the original sample weight. Degradation of the polymer sample under vacuum gave a residue at the bottom of the TVA tube representing 38.6% of the

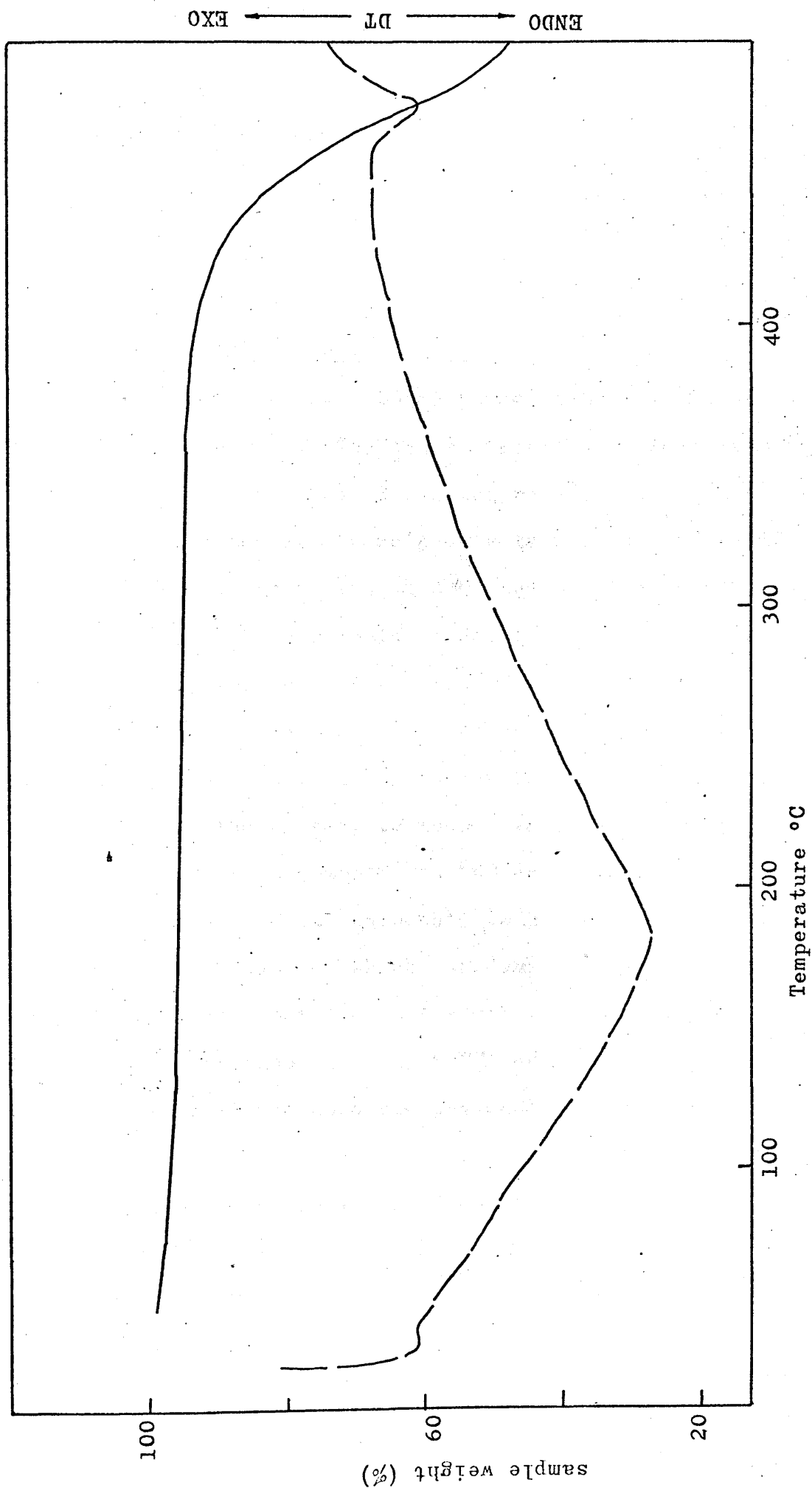


Fig. 6.2 TG and DTA curves for ZnPMA

original sample weight, 39.1% accumulated on the cooled upper part of the TVA tube and 6.5% was trapped as volatile liquid products.

Differential Thermal Analysis

The result of DTA for a 10 mg powder sample of ZnPMA is illustrated in Fig. 6.2. The trace exhibits two features, a plateau, which at the standard heating rate of 10°C/min starts around 50°C and peaks at the reference temperature of 185°C and an endotherm which starts at 430° and peaks at 455°C.

The plateau at 185°C could be due to release of absorbed moisture and precipitant because the IR spectrum of the residue at this temperature showed no change in the polymer structure. The endotherm at 455°C can only correspond to the decomposition of the polymer in such a way that ZnCO_3 is formed which in turn decomposes to ZnO as soon as it is formed. The decomposition of metal carbonate to metal oxide is a well known endothermic reaction which can dominate any exotherm occurring at that temperature. A similar phenomenon was observed in the decomposition of MgPMA as shown in Chapter 5. MgPMA and ZnPMA did not show the presence of metal carbonate at any stage of their degradation, but other divalent salts decomposed to metal carbonate as identified by IR.

Product Analysis

Gaseous product analysis was carried out by IR spectroscopy, and liquid volatile analysis by GLC.

Infrared analysis of the volatile products. The IR spectrum of the gaseous products of decomposition of ZnPMA below 500°C is shown in Fig. 6.3, and additional information is in Table 6.1. The major condensable gaseous products are carbon dioxide and dimethyl ketene. The essential features of the spectrum obtained have been discussed in Chapter 5. The condensable gases evolved during temperature programmed degradation at 10°C/min to 500°C, were distilled from the system into an IR cell (path length 10 cm) using the product collection apparatus described in Chapter 2. Gases which were condensable at -196°C under the continuous evacuation conditions employed in TVA were examined after degradation in a closed system. The IR spectrum obtained from degradation of ZnPMA to 500°C in a closed system is included in Fig. 6.3.

Quantitative measurements of carbon dioxide and dimethyl ketene were carried out by optical density measurements of IR absorptions at 2240 cm^{-1} and 2138 cm^{-1} respectively. The method employed was the same as described in Chapters 4 and 5 for similar products. The mole percentages of carbon dioxide and dimethyl ketene, per monomer unit of polymer, were found to be 9.19% and 0.3% respectively.

Gas liquid chromatography. The liquid volatile products obtained from degradation of ZnPMA to 500°C were identified by GLC; the variety of aldehydes and ketones present did not allow their positive identification by IR. GLC results employing both columns and conditions as described in Chapters

| Products Condensable at -196°C | Products Non-Condensable at -196°C |
|--|---------------------------------------|
| Carbon dioxide Dimethyl ketene Butene-1 Isobutene Propylene Ethylene Acetylene Toluene C=O, of ketones | Carbon monoxide Methane |

Table 6.1

Gaseous degradation products arising from ZnPMA
identified by IR spectroscopy.

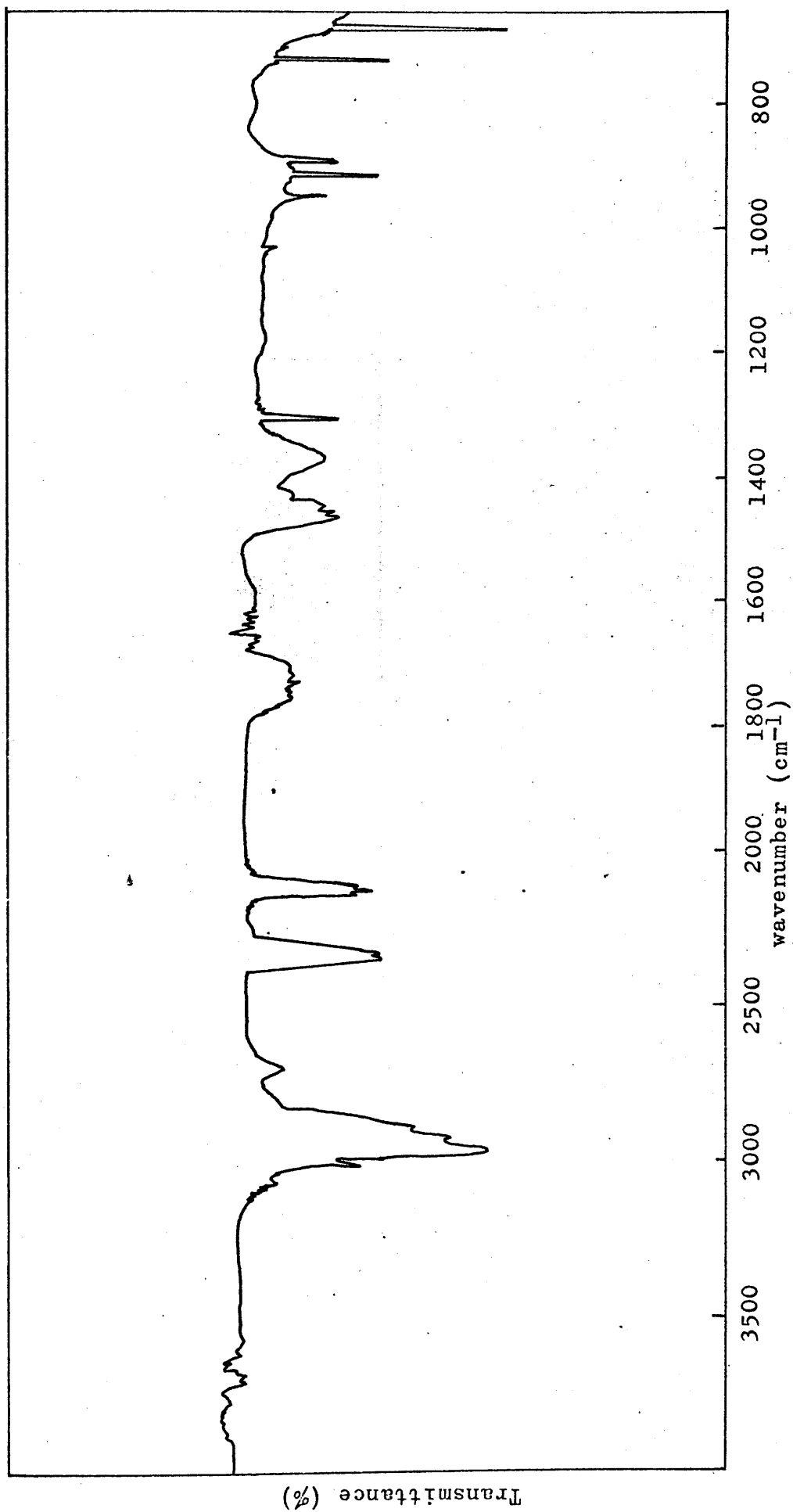


Fig. 6.3 IR spectra of gaseous volatile products from ZnPMA

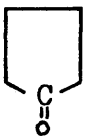
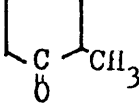
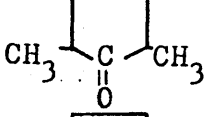
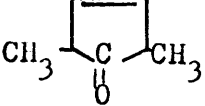
| Liquid volatiles | mole % per monomer unit |
|--|-------------------------|
| $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \cdot \text{CHO} \\ \diagup \\ \text{CH}_3 \end{array}$ | 0.99 |
| $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$ | 2.50 |
| $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \cdot \text{CO} \cdot \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array}$ | 0.28 |
| $\text{CH}_3 \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \text{CH}_3$ | 0.22 |
| $\text{CH}_3 \cdot \text{CH}=\text{CH} \cdot \text{COCH}_3$ | 0.38 |
| $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH} \cdot \text{COCH} \cdot \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array}$ | 0.27 |
|  | 0.32 |
|  | 0.47 |
|  | 0.70 |
|  | 2.95 |

Table 6.2

Major volatile liquid products

from degradation of ZnPMA

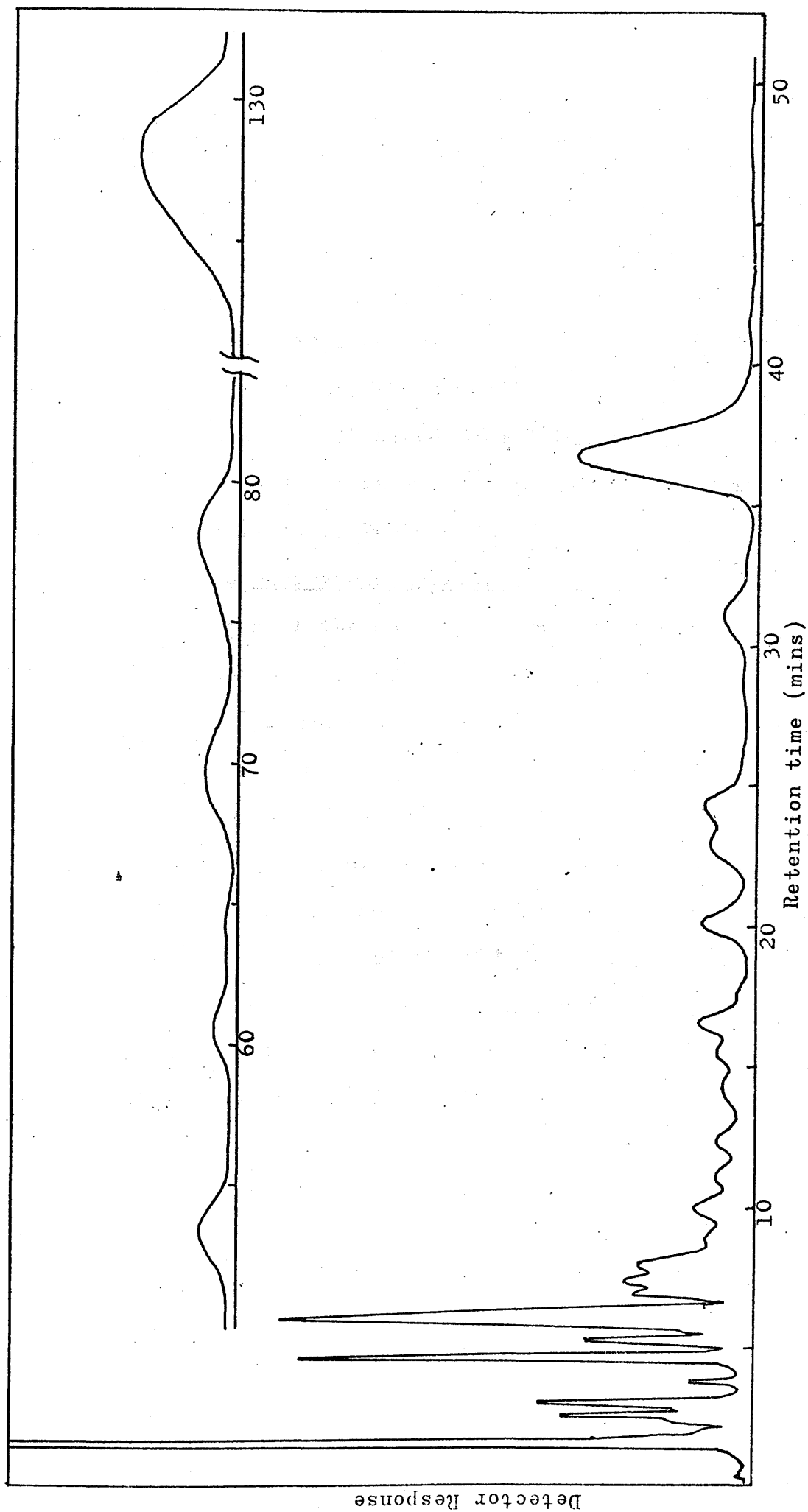


Fig. 6.4 GLC traces of liquid degradation products from ZnPMA

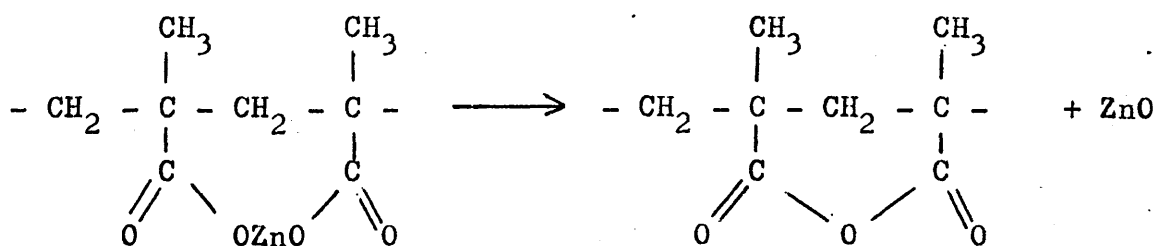
2, 4 and 5 confirmed the presence of products similar to those obtained from alkaline earth metal salts. The minor products identified by GLC were: acetylaldehyde, acetone, propionaldehyde, methacrolein, methyl ethyl ketone, benzene, methyl isopropylketone, toluene, mesityloxide and mesitylene. GLC traces of liquid volatile products obtained from ZnPMA degradation are shown in Fig. 6.4, and the mole percentages per monomer unit obtained are summarised in Table 6.2.

Structural Changes During Decomposition

The IR spectrum of the cold ring fraction (CRF) obtained from ZnPMA decomposition does provide the best insight into the structural rearrangements which can take place since this fraction consists of zinc metal as the major product with only a small amount of chain fragments. These chain fragments gave an IR spectrum consisting of two weak absorption bands at 1650 cm^{-1} and 1420 cm^{-1} and some very weak bands around 3000 cm^{-1} . The IR spectrum of the CRF was similar to those obtained from similar fractions arising from the degradation of other divalent metal salts, although this was the only instance in which metal was found as a deposit on the cold junction of the TVA tube. As was discussed in Chapter 5, these absorptions cannot be assigned to a particular compound but it may be assumed that the CRF may consist of a mixture of long chain hydrocarbons and fragments containing ketonic groups in the chain.

Fig. 6.5 illustrates the region of primary interest in the IR spectra of (a) ZnPMA, (b) the residue from ZnPMA degraded to 400°C, (c) the residue from ZnPMA degraded to 450°C, and (d) the residue from ZnPMA degraded to 500°C.

It is obvious from Fig. 6.5 that throughout the course of degradation the intensity of the carbonyl stretching vibration at 1560 cm^{-1} is decreasing and a new band around 500 cm^{-1} is appearing. This new band may be assigned to ZnO, as was confirmed by comparison with the reference spectrum of ZnO. The formation of ZnO during the decomposition could result either from the direct decomposition of polymer to ZnO or from secondary decomposition of ZnCO_3 which may be formed during degradation. If ZnO is formed direct from the polymer decomposition, then the residual polymer chain should consist of anhydride structures.



Sections (b), (c) and (d) of Fig. 6.5 do not show any absorption around 1800 , 1765 and 1020 cm^{-1} , which are usually assigned to polymethacrylic anhydride. This suggests that there is another route for the formation of ZnO and it could be from decomposition of ZnCO_3 . The spectra indicated above are not indicative of the presence of ZnCO_3 but it may decompose as soon as it forms. Dollimore⁹⁵ et al. degraded

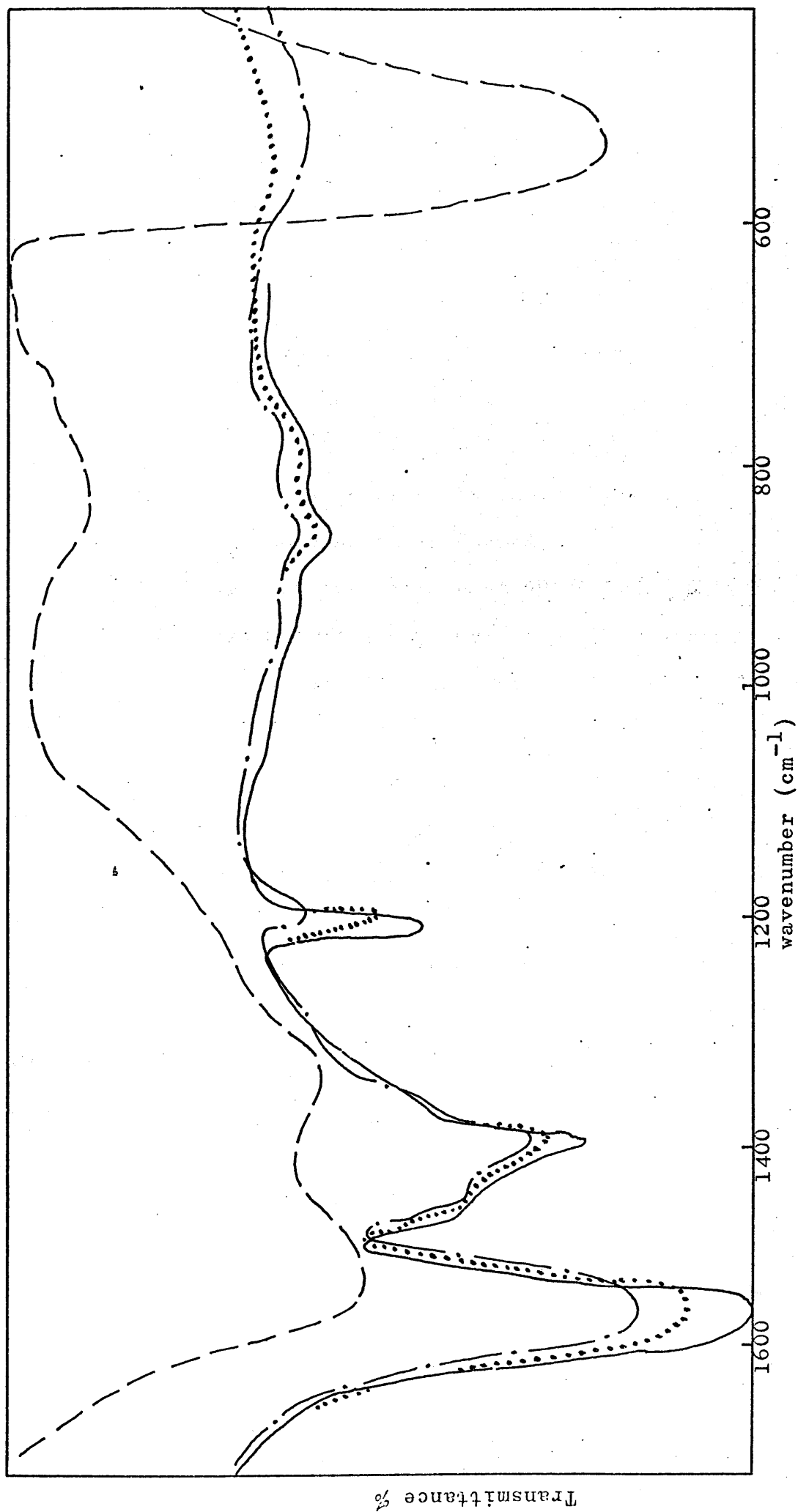


Fig. 6.5 IR absorption spectra of: — ZnPMA, ZnPMA degraded to 400°, --- ZnPMA degraded to 450° and to 500° and — — — ZnPMA degraded to 500°.

zinc oxalate and detected only the formation of ZnO during degradation. The stability of ZnCO_3 at a temperature of 450°C was investigated in the present studies and it was found to decompose completely to oxide under vacuum.

Metal isobutyrate was detected as a product during the degradation of other metal salts, but not in ZnPMA degradation. This discrepancy could also arise by the decomposition of zinc isobutyrate as soon as it is formed.

The IR spectrum of the residue at 500°C (Fig. 6.5(d)) also shows the presence of a carbonyl stretching vibration at 1550 cm^{-1} . This is regarded as indicative of the presence of some undegraded residual polymer, as the absorption at 1550 cm^{-1} is a major absorption in the spectrum of undegraded polymer (Fig. 6.5(a)), assigned to $-\text{CO}_2^-$ group.

Comparison of ZnPMA Degradation With Those of Other Divalent Salts.

The nature of the volatile products and structural changes which can occur during decomposition suggest a similar pattern of degradation, as discussed in Chapters 4 and 5. A few outstanding features exist among all the divalent metal salts;

- (a) The TVA trace for ZnPMA exhibits a T_{max} (424°C) lower than those of corresponding divalent metal salts.
- (b) ZnPMA gave 9.08 mole % of liquid products per monomer unit whereas MgPMA, CaPMA, SrPMA and BaPMA gave 12.05, 21.37, 19.76 and 15.64 mole %. This difference shows clearly the effect of the metal ion on the degradation of the salt.

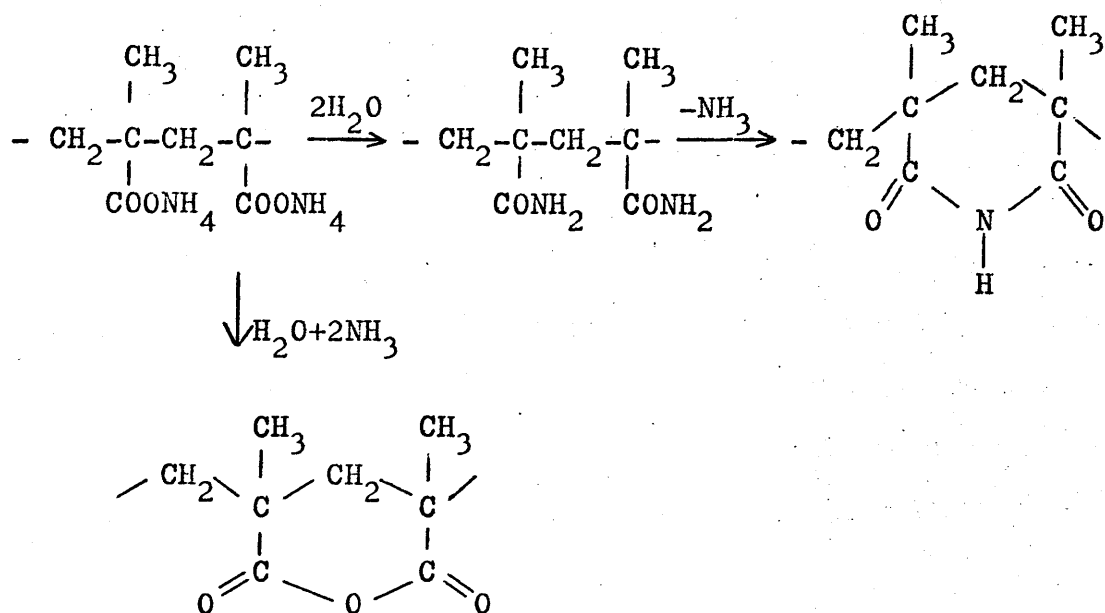
C H A P T E R S E V E N

THERMAL DEGRADATION OF AMMONIUM POLYMETHACRYLATE AND RELATED HOMOPOLYMERS

In the preceeding chapters some aspects of degradation of metal salts of polymethacrylic acid have been discussed. In this Chapter the decomposition of NH_4PMA will be described. It was found in present studies that structural changes during the decomposition of NH_4PMA were closely similar to those which may occur during the degradation of PMAA and PMAM. In the light of the results obtained, the thermal degradation of PMAA is reviewed and thermal behaviour of PMAM is discussed.

INTRODUCTION

In the literature, no previous attempt appears to have been made to study the thermal decomposition of NH_4PMA . It seems possible that cyclic anhydride and cyclic imide units may occur in the chain during its thermal degradation;



It is evident that support for such a mechanism may be gained from a study of PMAA and PMAM homopolymers, which are effectively an intermediate stage of the decomposition scheme outlined.

Thermal imidization has been carried out by a number of workers.^{29,96-98} Haas and MacDonald⁹⁸ have shown imidization to occur both during the polymerization and subsequently during thermal degradation of PAM and PMAM. Imide formation during polymerization will result in nitrogen deficiency in polymer analysis arising through escape of NH_3 from the system. The extent of this reaction has been found to vary according to polymerization conditions.

The degradation of poly (methacrylic acid) which was briefly discussed in Chapter 1, was first carried out by Bresler, Joton and co-workers²⁹ who found that cyclic

structures produced when water is liberated from PMAA are very much more thermally stable than the parent substance.

Grant and Grassie²⁵ studied the thermal decomposition of PMAA in greater detail and found that two separate reactions occur. The minor one is depolymerization to monomer which results in small yields of monomer (0.2%) while the major one is anhydride formation by elimination of H_2O between pairs of carboxylic acid groups. The residual polymer consists predominantly of six membered anhydride rings with occasional crosslinks.

Experimental

Monomer preparation and purification. Freshly distilled methacrylic acid was neutralized with NH_4OH (Richard Limited sp. G. 0.88). The technique of neutralization was similar to that employed in the preparation of metal salts as described in Chapter 3. The salt was precipitated in Analar acetone and filtered. It was further purified by dissolving in Analar methanol and precipitating in Analar anhydrous diethylether. It was dried under vacuum at room temperature for two hours and stored over silica gel in a dessicator. The salt was found to be very unstable as it started releasing ammonia at $40^\circ C$ under vacuum. Prolonged drying of the sample under vacuum at room temperature also leads to the decomposition of the salt to acid and ammonia.

Methacrylamide (Aldrich Chemical Co.) was recrystallized twice from hot toluene before drying under vacuum.

Polymerization

All polymerizations were carried out in solution. A brief account of these is given below and additional information is summarised in Table 7.1.

Ammonium methacrylate was polymerized in aqueous solution with hydrogen peroxide as initiator. The pH of the solution was raised by adding NH_4OH . The polymer was precipitated in Analar methanol, filtered, washed with acetone and purified by redissolving and reprecipitating. It was dried under vacuum at room temperature for 48 hours before subsequent analysis.

Methacrylamide and methacrylic acid were polymerised in sealed glass dilatometers using absolute ethanol (Burrough Ltd) as solvent with a monomer concentration of 2.5M. Polymethacrylamide separates out from monomer in ethanol while polymethacrylic acid was precipitated in petroleum ether. Polymethacrylamide was washed with hot ethanol to rid it of monomer, while PMAA was purified by redissolving in ethanol and precipitating in petroleum ether (40-60°). Both homopolymers were dried at 40°C under vacuum.

Determination of Nitrogen in PMAM and NH_4PMA ⁶⁶

The nitrogen contents of PMAM and NH_4PMA were determined by the Kjeldahl method. 300 mg of polymer were accurately weighed and transferred to a dry long necked kjeldahl flask. To the weighed sample, 10 ml of concentrated sulphuric acid, 3 g of sodium sulphate and a crystal of copper sulphate, were

added. The flask containing the above mixture was placed in the kjeldahl digestion unit and heated on a low flame for half an hour. As the frothing subsided the flame was turned up. The mixture was boiled gently to obtain a clear liquid. Further boiling was continued for two hours.

The contents of the flask were cooled and diluted with 300 ml of distilled water and neutralized with 40 ml of 50% sodium hydroxide. The solution was distilled into a beaker containing 50 ml of 0.1 N HCl and a few drops of phenolphthalein indicator. The distillation was carried out for 30 minutes to obtain 300 cc of distillate. The excess acid in the beaker was titrated with 0.1 N NaOH and from the amounts of 0.1 N HCl used to absorb the ammonia, the nitrogen contents of the sample were calculated.

Ammonium polymethacrylate and polymethacrylamide gave values of N content of 12.6% and 15.8% compared with the theoretical values of 13.58% and 16.5% respectively.

These low values may be ascribed to the following considerations;

- a. The addition of concentrated H_2SO_4 into the flask containing the sample could cause a sudden reaction and loss of ammonia may occur.
- b. NH_4PMA may have lost some ammonia during the polymerization and drying process and thus may have some acid units in the chain. These acid units, if present, are so small in number that they were not observed in the IR spectrum of the polymer.

| Polymer | Monomer Concentration | Solvent | Initiator Concentration | Temperature °C | Atmosphere | Time Hours | Yield |
|---------------------|-----------------------|---------|---|----------------|----------------|------------|--------|
| NH ₄ PMA | 5.1M | Water* | H ₂ O ₂ (30%) 1% v/v | 25 | N ₂ | 5.0 | 10.12% |
| PMAM | 2.5M | Ethanol | AIBN 0.05% w/v | 60 | vacuum | 2.0 | 9.20% |
| PMAA | 3.0M | Ethanol | AIBN 0.05% w/v | 60 | vacuum | 1.0 | 15.3% |

Table 7.1

Polymerization data

* Polymerized at pH 11.2

c. The low value of N content obtained from PMAM could be due to intramolecular loss of ammonia during polymerization as mentioned earlier. Haas and MacDonald⁹⁸ found 14.5% N compared with the theoretical value of 16.5% N. This was attributed to imidization during polymerization.

Results and Discussion

Thermal volatilization analysis

Figures 7.1, 7.2 and 7.3 illustrate the TVA curves for 50 mg powder samples of NH_4PMA , PMAM and PMAA respectively. The homopolymer samples were heated to 500°C at the rate of $10^\circ\text{C}/\text{min}$ under the normal conditions of TVA. The TVA behaviour of NH_4PMA (Fig. 7.1) is indicative of two distinct modes of degradation. Volatilization begins below 100°C and the limiting rate up to 1.4 mv observed in the -75° trace in the region up to 247°C is characteristic of water in the TVA system;⁴⁶ this is probably due to dehydration. Fig. 7.1 also shows that the -100° trace leaves the base line at the temperature of degradation of 100°C and returns to base line at 280°C . This may be due to evolution of ammonia which was identified in the products from this region. After the maximum rate of volatilization at 247°C (T_{max}), a small amount of volatile material is still given off, probably water since only 0, -45 and -75°C traces exhibit volatilization. This could be the result of dehydration of residual amide groups produced in the initial stage of degradation or intramolecular reaction of acid and amide groups. Further onset

of degradation occurs at 360° and T_{\max} is reached at 435°C . The TVA behaviour at this peak is typical of extensive polymer fragmentation. The presence of non-condensables in the TVA system accounts for the peak in the -196°C trace.

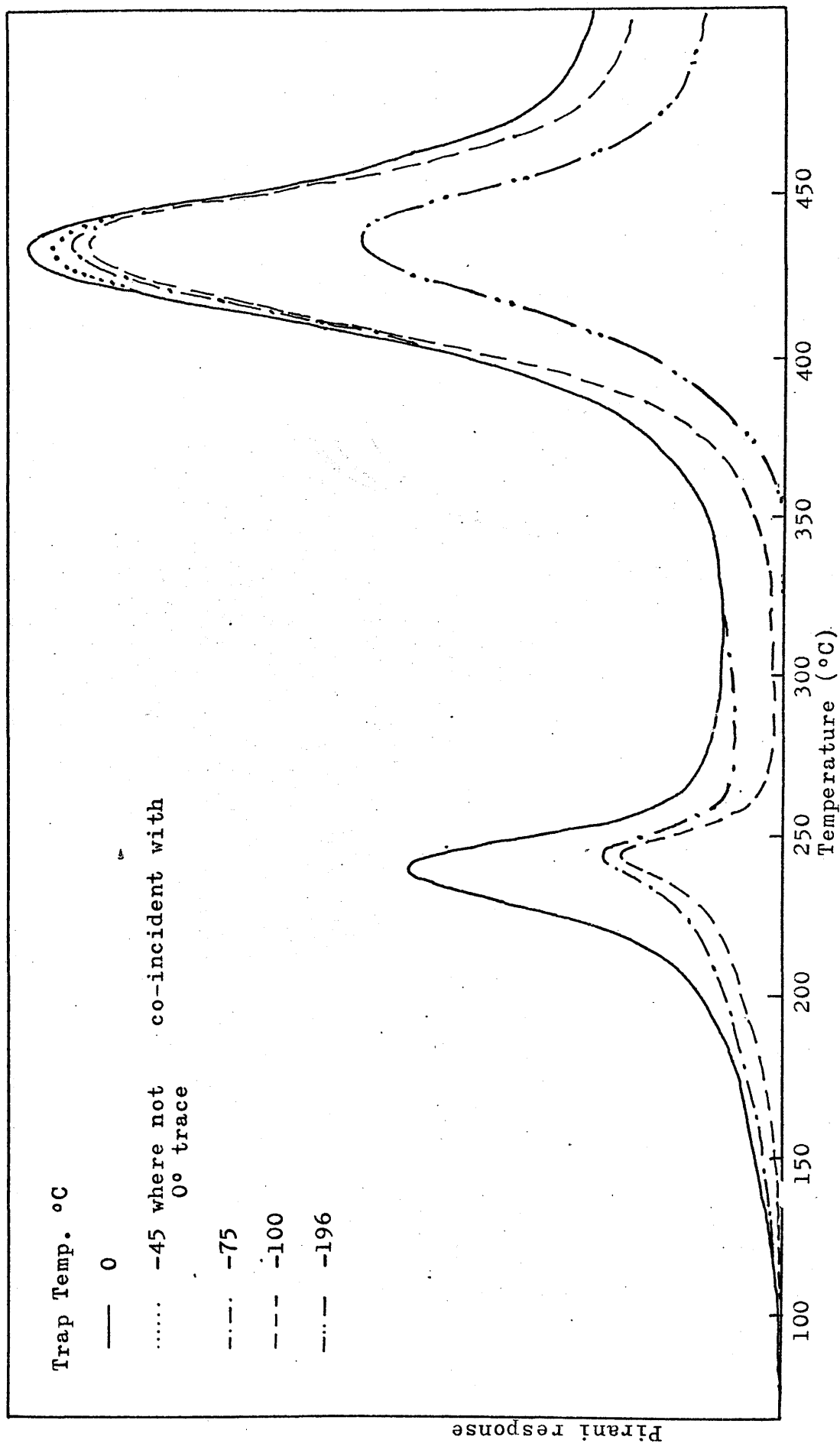
Two distinct modes of decomposition are evident in the TVA curve obtained for PMAM (Fig. 7.2). The initial stage gives rise to gaseous products volatile at all trap temperatures except -196° . Within the temperature range of the first peak ammonia and trace amounts of water were detected. At temperatures above about 310°C products which are non-condensable at -196° are evolved in addition to material exhibiting differential condensability in the -100° trap. In addition extensive chain scission occurs between 360 – 450°C resulting in a yellow cold ring fraction. Thus the first TVA peak could be the result of intramolecular imidization and the second may result from the decomposition of cyclized chain. The broadness of the second peak suggests a complex process which may result from the condensation of residual amide groups and cyclic imide rings.

The TVA trace for PMAA is shown in Fig. 7.3 and is identical to that obtained by McNeill⁴⁵ who interpreted it in the following way. Slow release of volatile material begins as soon as the temperature starts to rise. This gradual release is consistent with the view that this material is water absorbed by the polymer.²⁵ The low plateau of the -75° trace is characteristic of water. A more extensive volatilization

| Polymer | First peak T_{\max} | Second peak T_{\max} |
|-------------------------|--------------------------|---------------------------|
| NH_4PMA | 247°C | 435°C |
| PMAM | 295°C | 405°C |
| PMAA | 245°C | 440°C |

Table 7.2

Details of TVA thermograms - Figures 7.1-7.3

Fig. 7.1 TVA curve for NH_4PMA

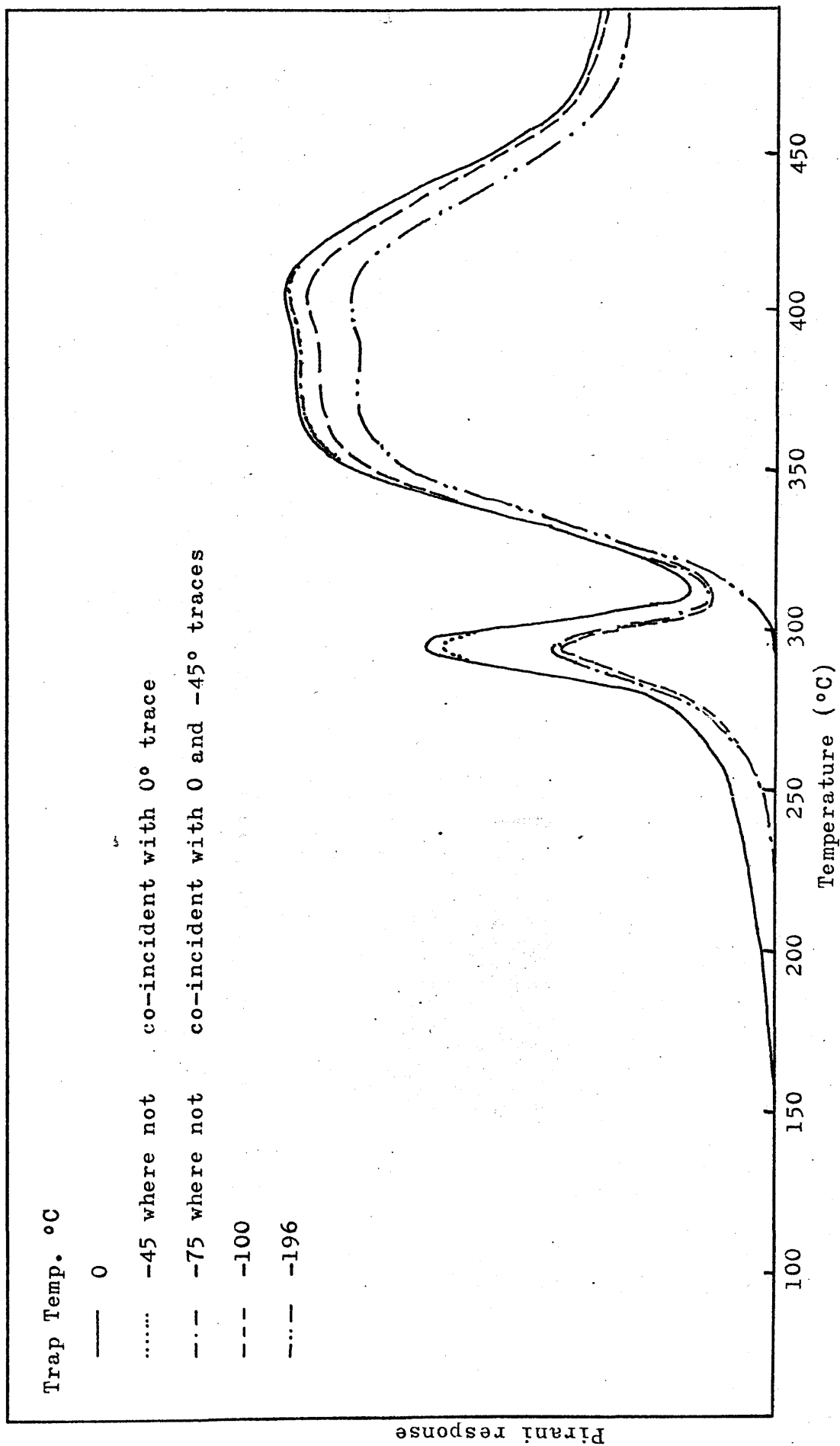


Fig. 7.2 TVA curve for PMAM

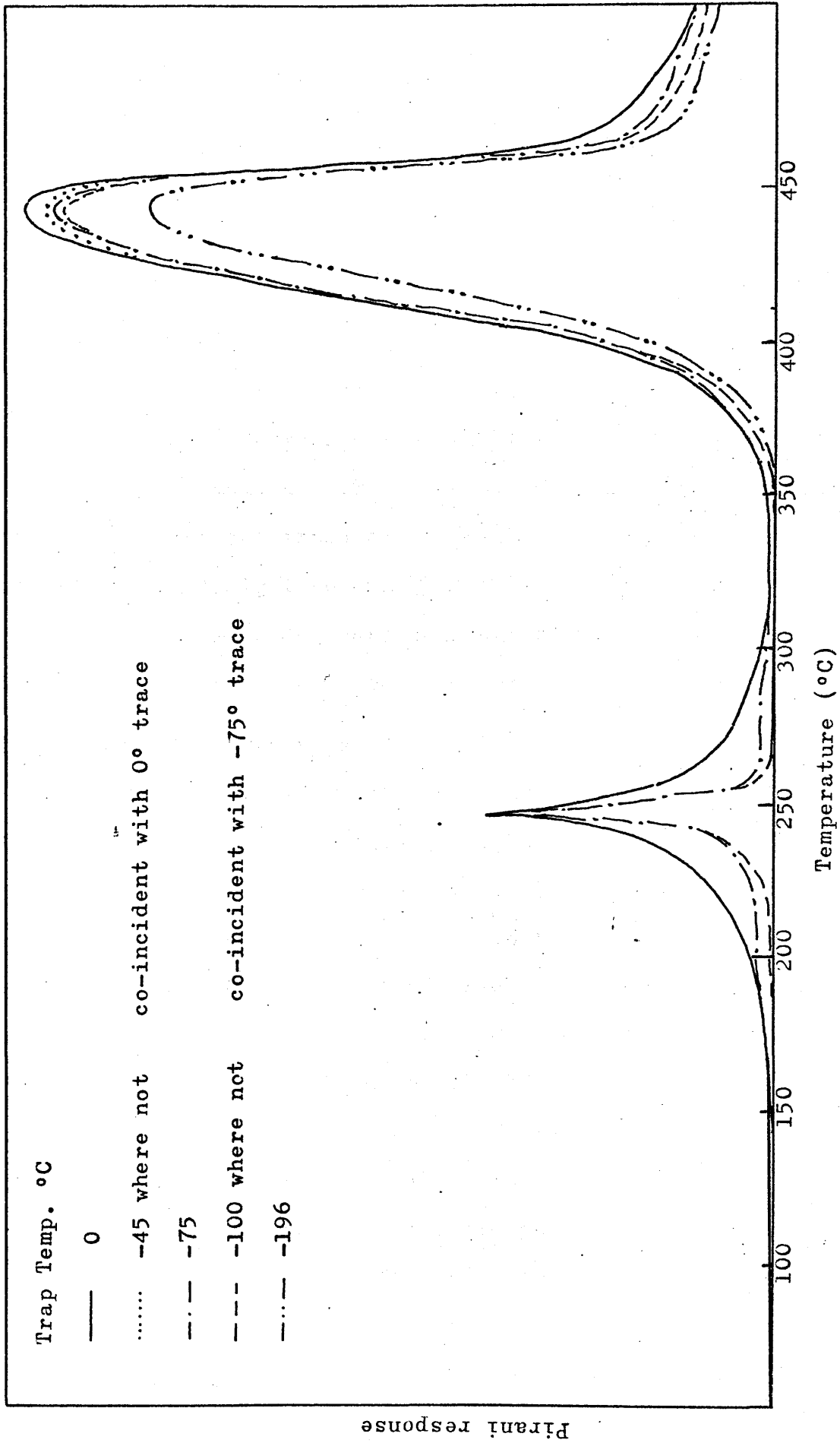


Fig. 7.3 TVA curve for PMAA

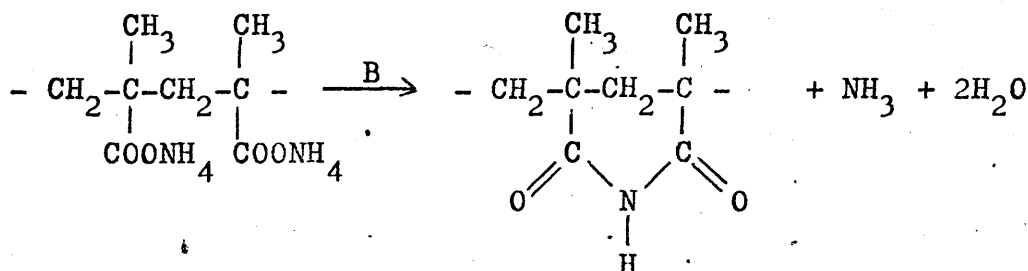
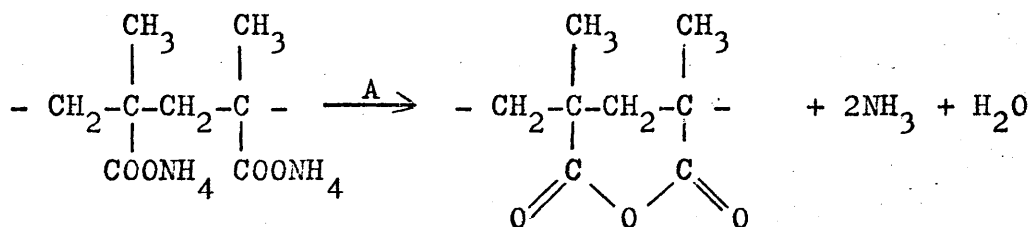
starts at 200°C, indicating that greater amounts of water are being produced. The almost concurrent evolution of a material volatile at -100°C (with the consequent displacement of -75° trace until this volatilization is complete) is due to the precipitant, ether. At 300°C the 0° and -45° traces return to base line, indicating that water evolution has ceased. At this temperature, further evolution of volatiles commences rising to a maximum rate (T_{\max}) at 440°C. The anhydride ring structures which are expected to result after the loss of water (1st peak) might be expected to yield highly volatile products carbon dioxide, carbon monoxide and hydrocarbons, thus accounting for the response after the -196°C trap.

Thermogravimetric Analysis

TGA thermograms were obtained using a heating rate of 10°C/min in a dynamic nitrogen atmosphere. Prior to each experiment the sample was preheated at 50°C under nitrogen to remove absorbed moisture. Fig. 7.4 illustrates the results for the polymers NH_4PMA , PMAM and PMAA and additional details are given in Table 7.3.

The TGA curve for NH_4PMA exhibits a two stage weight loss concurrent with the evolution of gaseous products observed in TVA experiments. The initial weight loss corresponds to 27.5% of the original sample weight, while the formation of volatile chain fragments and further gaseous products comprises 62.5%. The remaining 10% of the original sample weight is the black, involatile and insoluble residue.

Consideration of the possible imidization and formation of anhydride cyclic structures leads one to assume two possible extents of decomposition which may occur during the initial weight loss in NH_4PMA , namely:

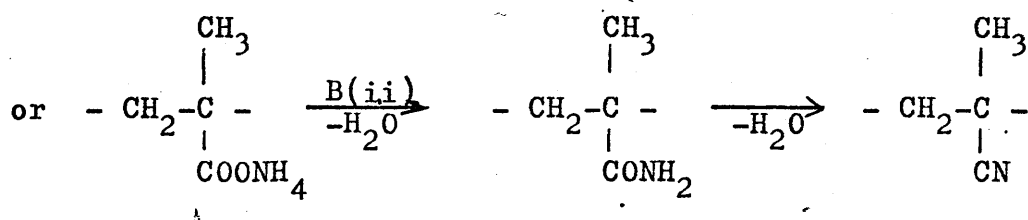
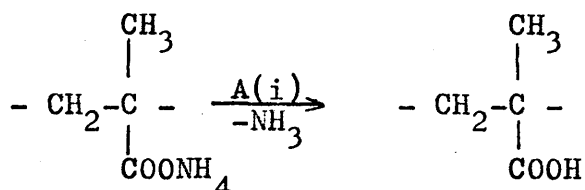


The reactions A and B seem to be unlikely to go to 100% cyclization. Marvel and co-workers^{99,100} have shown that approximately 85% of the groups of poly (methyl vinyl ketone) undergo a thermal intramolecular condensation. The removal of chlorine by zinc from poly (vinyl chloride) obeys Flory's statistical calculation,^{101,102} which predicts isolation of 13.53% of the substituents. Thus if weight losses can be corrected by Marvel's approach then the calculated values of these for reactions A and B should be as follows:

$$\text{A} = 21.6\%$$

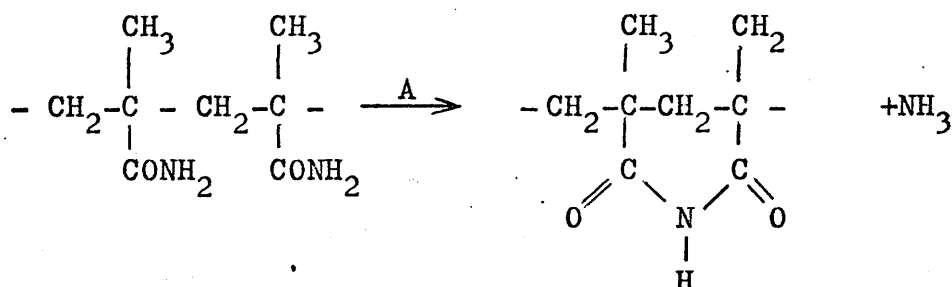
$$\text{B} = 21.9\%$$

The experimental weight loss was found to be $27.5\% \pm 2$. This $\pm 2\%$ error is due to the amount of moisture absorbed by the polymer. The experimental weight loss is in excess of that calculated, beyond the limit of experimental error. This suggests that the decomposition of isolated monomer units also occurs:

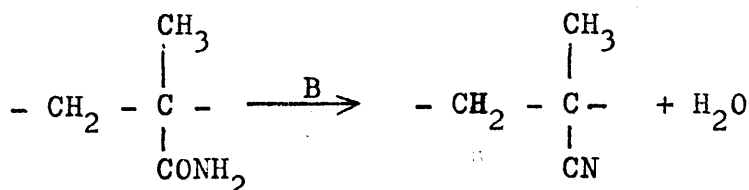


If 15% monomer units are isolated then weight losses per unit for these processes should be: (i) 2.4%, (ii) 5.2%. The combination of reactions A, A(i) and B, B(ii) would give the total calculated weight loss, 24.0% and 27.3%. Similarly the combination of reactions A(ii) and B(i) would give weight loss 26.8% and 24.3% respectively. These values are close to the experimental one, thus it is difficult to draw a definite conclusion. These reaction possibilities will be discussed further in the later part of this Chapter.

PMAM (Fig. 7.4) again exhibits a two stage weight loss. The initial 14.0% loss may be due to imidization with evolution of ammonia. The final weight loss comprises 66.0%, a result of volatile chain fragmentation and further gaseous products. The remaining 19% of the original sample weight is the black, involatile and insoluble residue. Considering the possible imidization at the initial decomposition, the reaction could be written as:

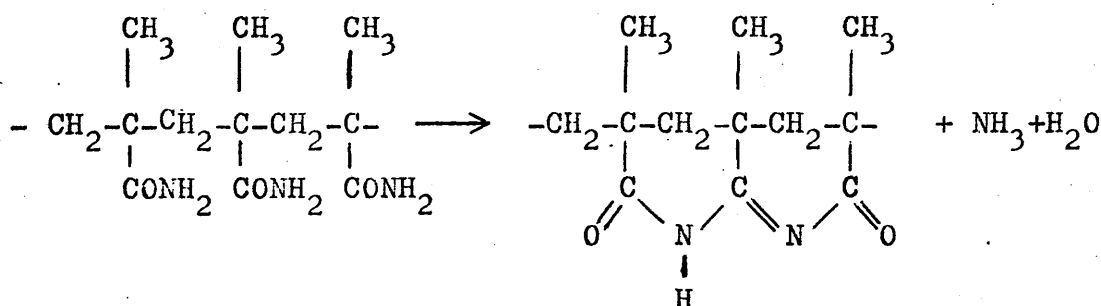


Again if the weight loss for reaction A could be corrected for isolated unreacted units on the basis of Marvel's approach, then it should be 8.5%, which is 5.5% less than the experimental value of 14.0% at the initial stage of degradation. If the uncyclized monomer units (15%) lose water this would give rise to a further weight loss of 3.18%.



The combination of reactions A and B gives the total calculated weight loss 11.68%, less than the experimental 14.0%. Within the limit of 1.5% experimental error, the

calculated values of weight losses, are in fair agreement with the experimental result. Grassie and Samson¹⁰³ have briefly studied the degradation of PMAM and found similar weight losses. They have proposed an intramolecular imidization with two possible extents of decomposition. In addition to the simple cyclization with loss of ammonia which has been described earlier, the following more complex cyclization reaction may also take place:



This reaction gives 16.7% weight loss, thus any minor contribution by such a reaction, could increase the calculated weight loss.

The TGA curve from PMAA (Fig. 7.4) shows that there are three distinct regions of weight loss: the initial 3% loss of absorbed water, the subsequent 12.00% weight loss of water (from dehydration reaction) and precipitant and the final large weight loss due to chain fragmentation of the residual polymer, leaving a residue of 10.90% of the original sample weight at 500°C. The recorded weight loss for anhydride formation is 12.00% which is more than the theoretical weight

| Polymer | Weight loss (%) | | Residue weight (%) |
|---------------------|-----------------|-------------|--------------------|
| | Initial stage | Final stage | |
| NH ₄ PMA | 27.5 | 62.5 | 10.0 |
| PMAM | 14.0 | 67.0 | 19.0 |
| PMAA | 12.0 | 77.1 | 10.9 |

Table 7.3

TGA data for NH₄PMA, PMAM and PMAA

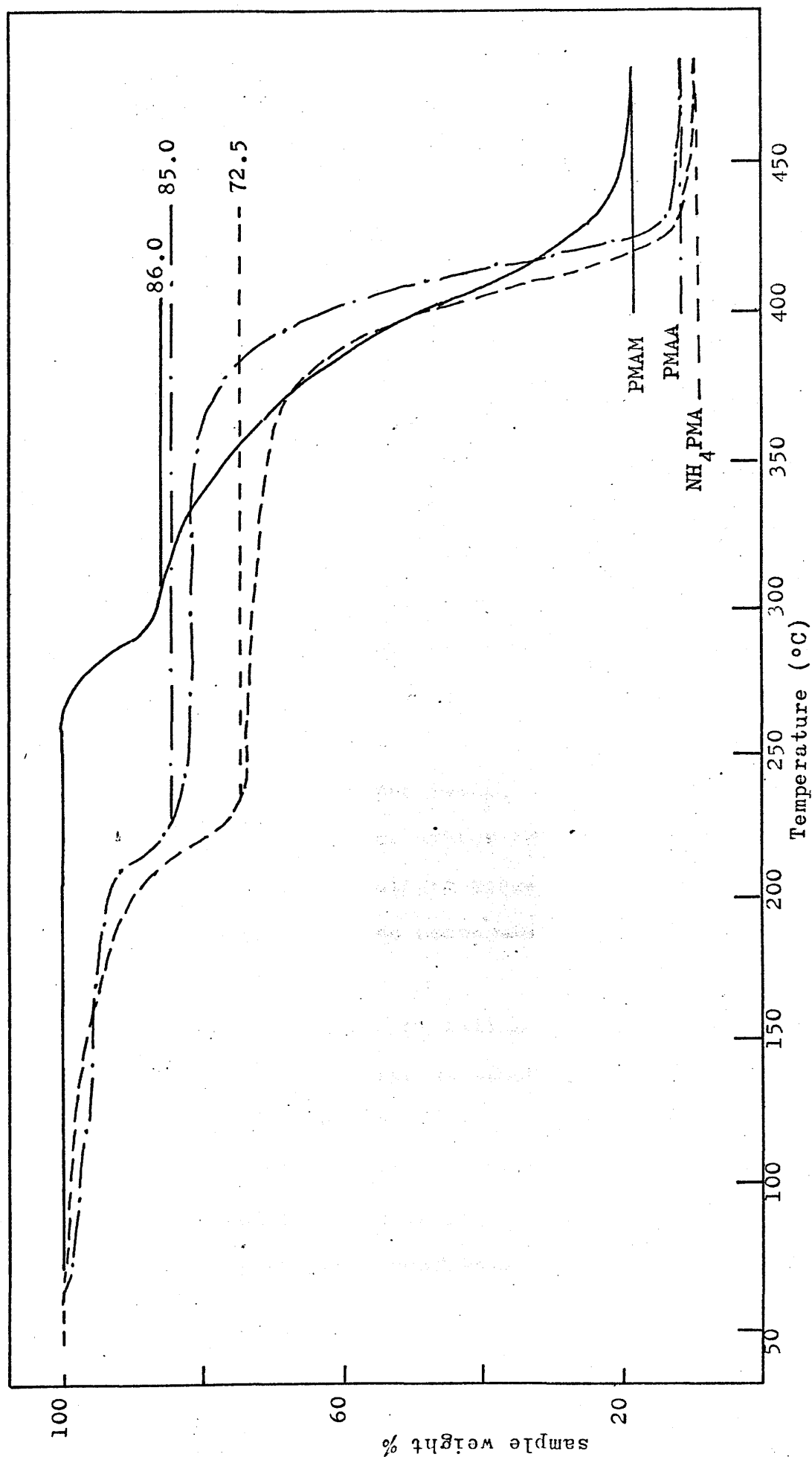


Fig. 7.4 TG curves for NH_4PMA , PMAM and PMAA; Dynamic N_2 atmosphere, heating rate $10^{\circ}\text{C}/\text{min}$

loss (10.47%). This difference could be due to precipitant retained by the polymer sample.

Differential scanning calorimetry

Figure 7.5 illustrates the DSC curves for 5 mg powder samples of NH_4PMA , PMAM and PMAA. The polymer samples were preheated at 50°C in the DSC cell under a dynamic nitrogen atmosphere prior to these experiments.

The DSC curve for NH_4PMA has an endotherm around 225° associated with the loss of ammonia and water to result in initial cyclization. The second broad endotherm at 425°C occurs during fragmentation of the residual modified chain.

Again, two endotherms are evident in PMAM at 280° and 420° corresponding to the initial cyclization and later fragmentation processes, respectively.

Similarly, two endotherms appear in PMAA at 237° and around 450°C . The first endotherm seems to be complex, as release of precipitant is also accompanied by H_2O evolution (due to dehydration).

It is evident that the cyclization reaction in all three homopolymers occurs at a different temperature. The ease of cyclization is in the sequence in $\text{NH}_4\text{PMA} > \text{PMAA} > \text{PMAM}$. Ammonium polymethacrylate contains carboxylate ion along the chain and because of these polar groups, the chain is expected to have an extended configuration. On the other hand, PMAA may have less extended and PMAM a coiled configuration. These factors may account for the observed differences.

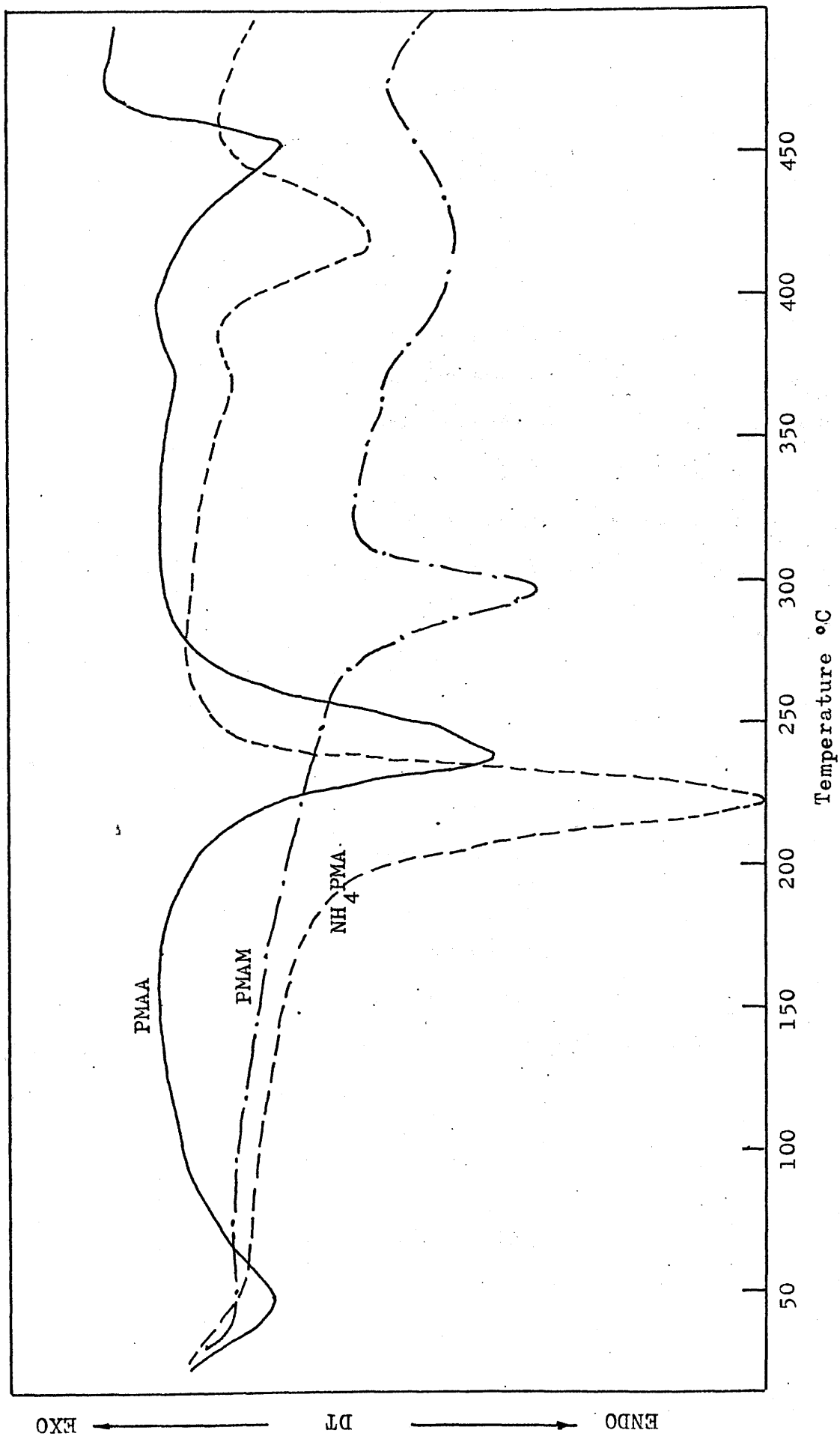


Fig. 7.5. DSC curves for NH_4PMA , PMAM and PMAA; dynamic N_2 atmosphere, heating rate $10^{\circ}\text{C}/\text{min}$

Product analysis. Volatile products were examined after degradation of 100 mg powder samples under the normal conditions of TVA. Cold-ring fraction spectra were obtained as chloroform solutions, and the percentage yield by weight was found by weighing the TVA tube before and after degradation. The quantitative yields of CRF are given in Table 7.4 and the regions of primary interest in the spectra are shown in Fig. 7.6.

Fig. 7.6(a) illustrates the spectrum of the CRF obtained from PMAM and shows the major carbonyl absorption to occur around 1690 cm^{-1} with both amide I and amide II bands at 1650 cm^{-1} and 1600 cm^{-1} respectively. Such bands are normally associated with cyclic amides, e.g. glutarimide.¹⁰⁴

IR spectrum of the CRF from PMAA (Fig. 7.6(b)) shows the presence of anhydride structures, since C=O absorption at 1800 cm^{-1} , 1755 cm^{-1} and 1700 cm^{-1} are usually assigned to six-membered cyclic rings.²⁵ These absorptions are also accompanied by the C-O-C stretching absorption at 1022 cm^{-1} . At 1600 cm^{-1} a sharp peak appears which may be assigned to a conjugated double bond (C=C-C=O); this is further confirmed by the double bond bending vibrations at 925 cm^{-1} , 875 cm^{-1} and 845 cm^{-1} . Thus these bands may indicate the presence of some unsaturation in the structures.

The IR spectrum (Fig. 7.6(c)) of CRF obtained from NH_4PMA has many features found in the spectra obtained from the corresponding products from PMAM and PMAA. The strong band at 1690 cm^{-1} in PMAM and weak band at 1700 cm^{-1} in PMAA is replaced by a strong and broad absorption in the CRF of NH_4PMA .

Thus ammonium polymethacrylate gave products with features similar to those for PMAM and FMAA.

Analysis of gaseous volatiles was carried out by IR spectroscopy. The TVA traces, TGA and DSC curves have shown two modes of decomposition for all three homopolymers, thus products evolved at two different stages were examined separately.

Initial stage degradation products. Ammonium polymethacrylate degraded to 320°C at the rate of 10°C/min in the TVA apparatus gave ammonia and water. The former was identified by IR spectroscopy and quantitative measurement was obtained by optical density measurement of the absorption at 931 cm^{-1} after collection of the total gaseous products in a 10 cm path length gas cell. The calibration plot of optical density against pressure as given in Chapter 2 was used to obtain weight percentage of ammonia. The possible initial cyclization reactions proposed led to calculated amounts of ammonia in reactions A, A(i), B and B(ii) equal to 14.03%, 7.01%, 3.0% and 0.0% respectively. The observed amount of ammonia was found to be 6.7% by weight, in close agreement with reaction B. Any minor contribution by the reaction proposed B(ii), A and A(i) cannot be ruled out at this stage and these will be discussed subsequently.

PMAM degraded up to 300°C at the heating rate of 10°C/min, evolved 5.57% of ammonia. The calculated amount of ammonia, which can be obtained from reaction A, proposed for PMAM should be 8.50% by weight. This value of ammonia yield is

based on Marvel's ^{99,100} approach assuming that only 85% of total monomer units can be cyclized. As in this case the calculated amount is far more than the experimental values; the number of cyclized units may be less than 85%. The experimental amount of ammonia (5.57%) suggests that the order of cyclisation is 60%.

Polymethacrylic acid degraded at 10°C/min to 300°C gave water as the product.

Final stage degradation products. After the initial stage of decomposition, the polymers were heated to 500°C and IR spectra of gaseous products and of a dried CHCl_3 solution of the liquid products were obtained. The liquid products showed traces of MAA from PMAA, and methacrylonitrile and water from NH_4PMA and PMAM. IR spectra of gaseous products obtained from three homopolymers are shown in Fig. 7.7, 7.8 and 7.9 and the fundamentals assigned to a particular volatile are listed in Table 7.5, confirmed by obtaining reference spectra. Quantitative measurements of HCN, CO_2 , HNCN and isobutene were obtained by optical density measurements of IR absorption at 714 cm^{-1} , 2349 cm^{-1} , 2280 cm^{-1} and 890 cm^{-1} respectively. Weight percentages of these volatiles obtained are given in Table 7.4 along with other quantitative data.

It is evident that HNCN, HCN and isobutene are predominant products from degradation of NH_4PMA . Small amounts of carbon dioxide are also evolved which may be accounted for by anhydride formation during the initial stage of degradation.

PMAM gave HCN (0.42%), isobutene (0.87%), NH_3 (0.8%) and

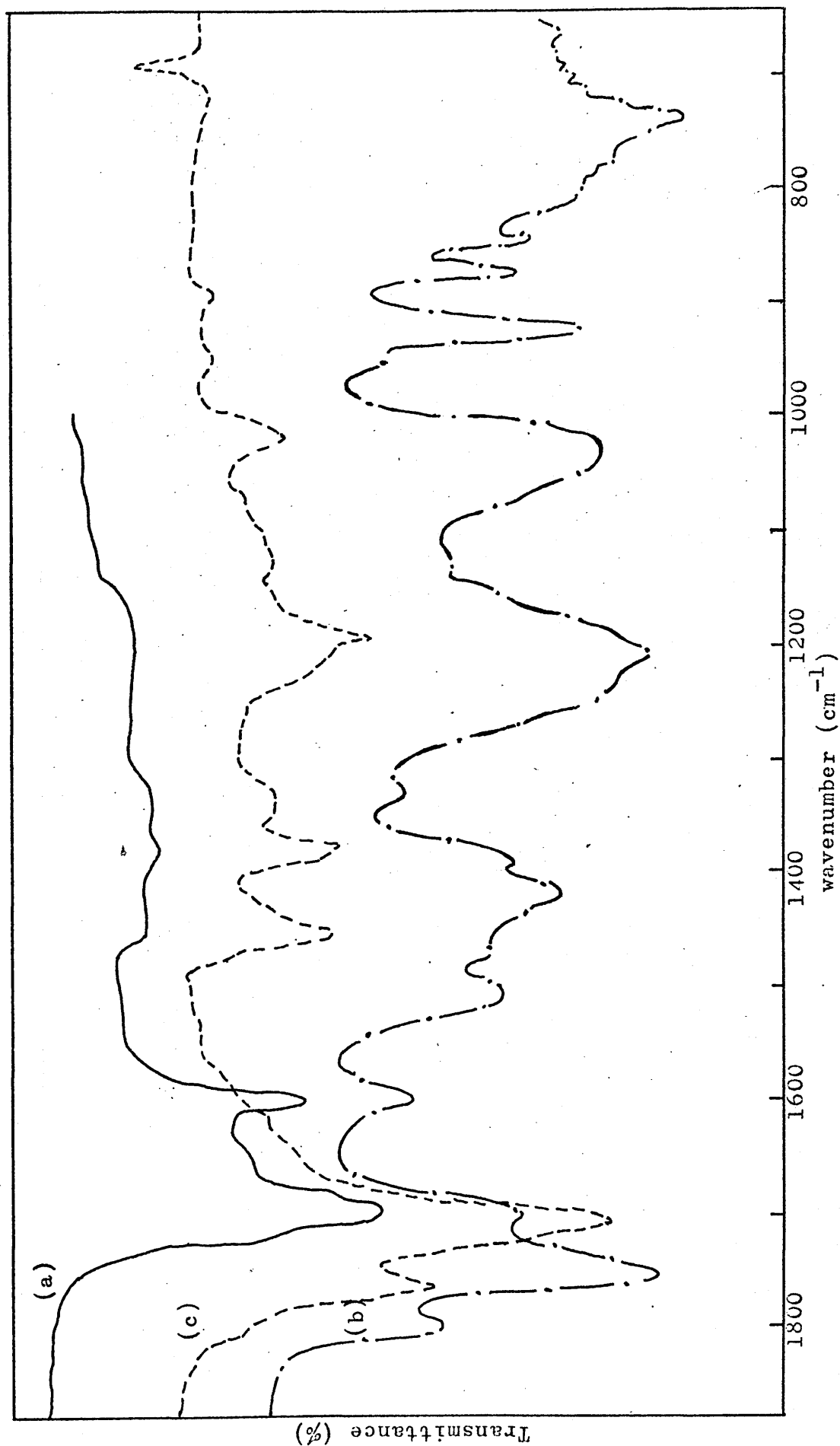


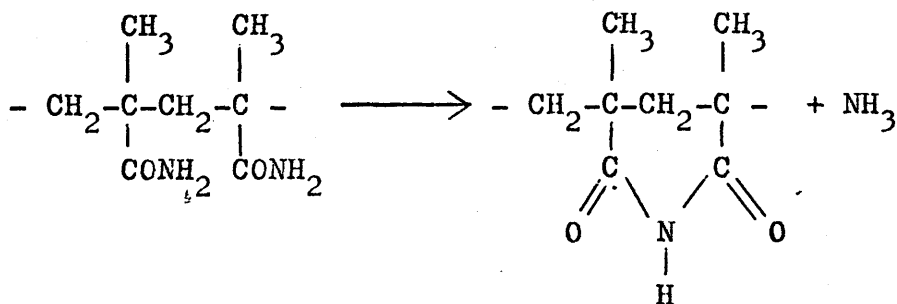
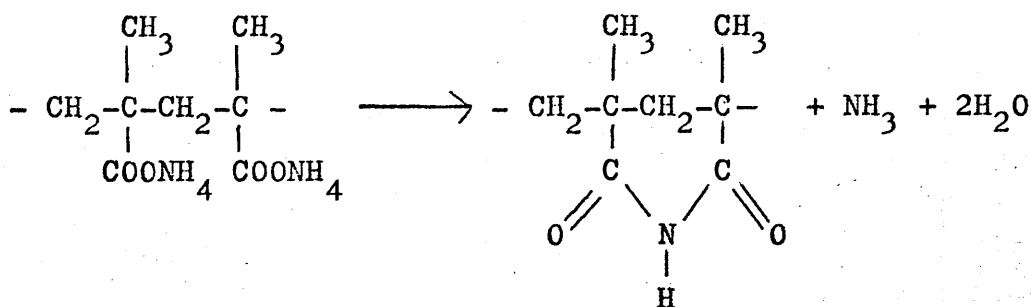
Fig. 7.6 IR absorption spectra of cold ring fractions at 500°C from; (a) PMAM, (b) PMAA, (c) NH_4PMA

| Polymer | weight percentage of product | | | | | |
|---------------------|------------------------------|------|-----------|------|-----------------|------|
| | NH ₃ | HCN | Isobutene | HNCO | CO ₂ | CRF |
| NH ₄ PMA | 6.7 | 1.67 | 0.64 | 8.2 | trace | 54.4 |
| PMAM | 6.3 | 0.42 | 0.27 | - | trace | 56.1 |
| PMAA | - | - | 1.37 | - | 11.6 | 49.4 |
| | | | | | | 5.0 |
| | | | | | | 19.0 |
| | | | | | | 12.0 |

Table 7.4

Quantitative Product Analysis of NH₄PMA, PMAM and PMAA

trace amounts of carbon dioxide. NH_4PMA gave substantial amounts of HNCO but this did not appear in the products from PMAM , although a similar type of initial cyclization was postulated:



The explanation for this discrepancy in PMAM could be that residual amide units after initial cyclization produce further amounts of ammonia in the final stage of degradation which could neutralize HNCO or any other acid present among the volatile products. Further evidence was obtained by degrading NH_4PMA to 500°C and collecting the total products of both stages. The IR spectra obtained (Fig. 7.7(b)) showed the absence of HNCO and reduced amounts of HCN . Though ammonium isocyanate, which can be formed from neutralization

| Frequency (cm^{-1}) | Assigned to a compound |
|--------------------------------|------------------------|
| 2339-2345 | carbon dioxide |
| 2260-2280 | isocyanic acid |
| 2080-2150 | carbon monoxide |
| 1740,1640,1220 | methacrylic acid |
| 1140 | - |
| 1310 | methane |
| 949 | ethylene |
| 940 and 958 | ammonia |
| 927 | methacrylonitrile |
| 890 | isobutene |
| 721 and 669 | carbon dioxide |
| 713 | hydrogen cyanide |

Table 7.5

Frequencies assigned to a particular compound, from spectra shown in Figs. 7.7, 7.8, 7.9 and 7.10.

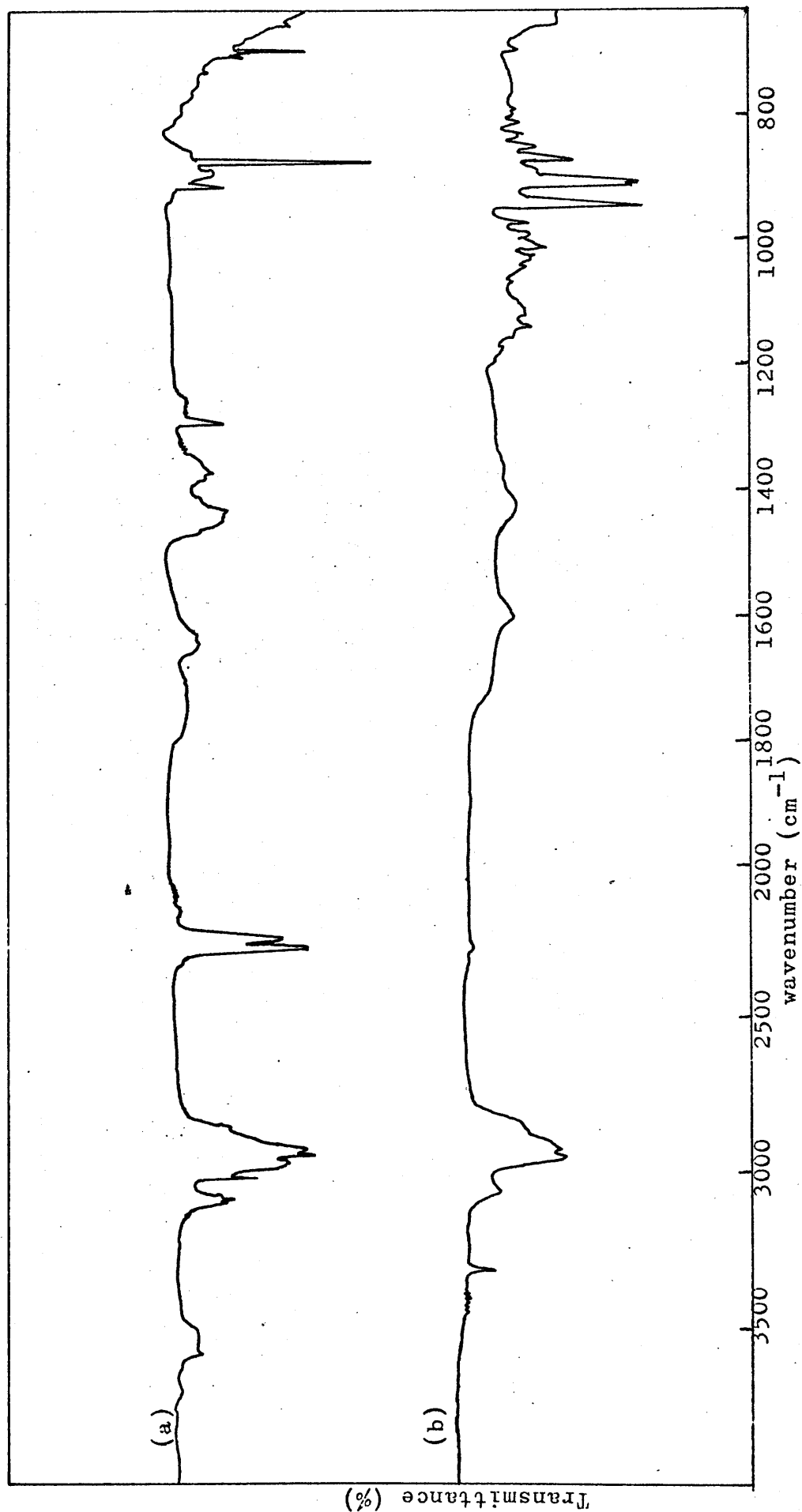


Fig. 7.7 IR spectra of gaseous volatiles from NH_4PMA ; (a) final stage products (320–500°C), (b) total volatiles (r.t.–500°C) (initial and final stage).

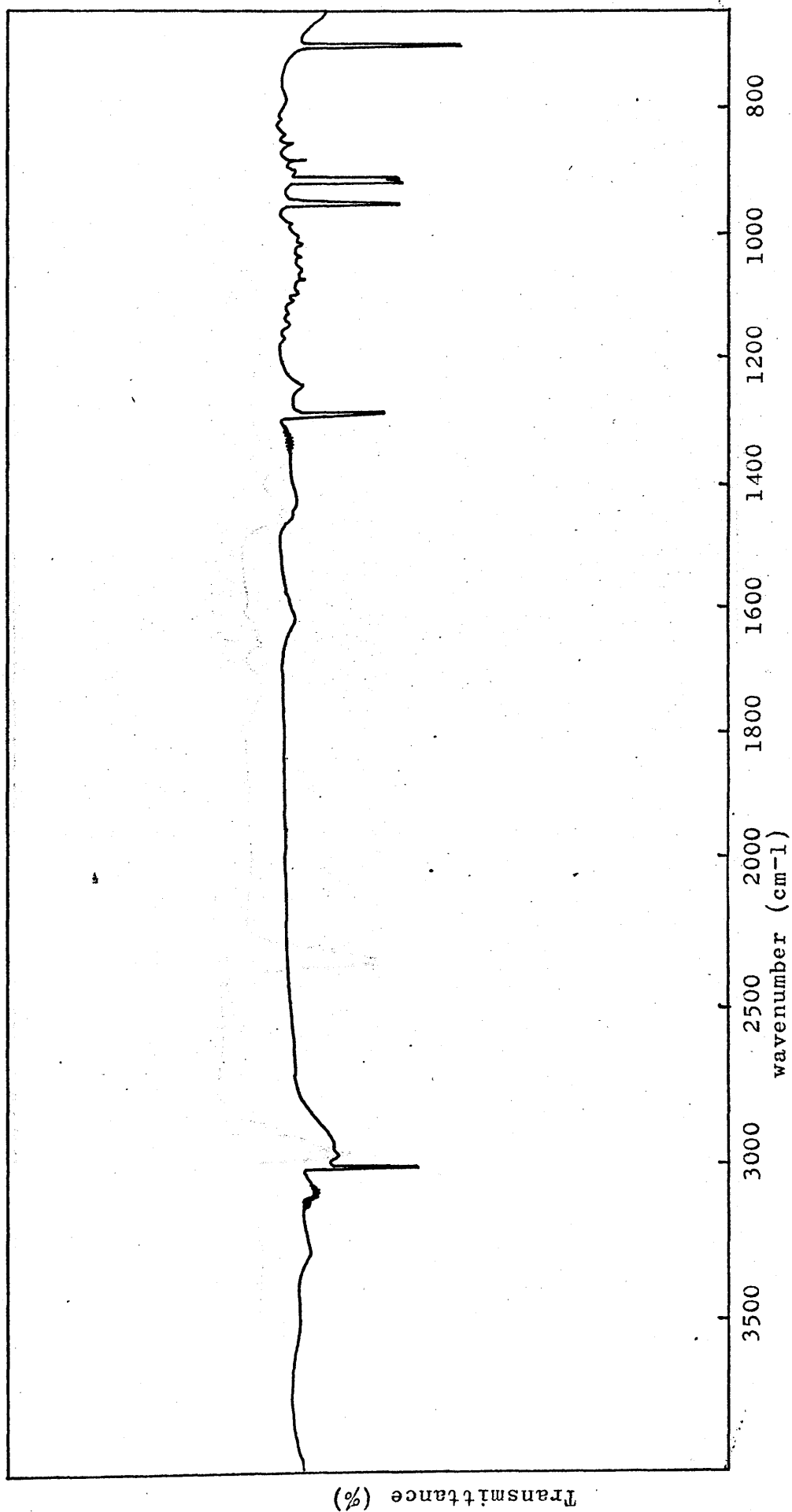


Fig. 7.8 IR spectrum of gaseous volatile products from PMAM

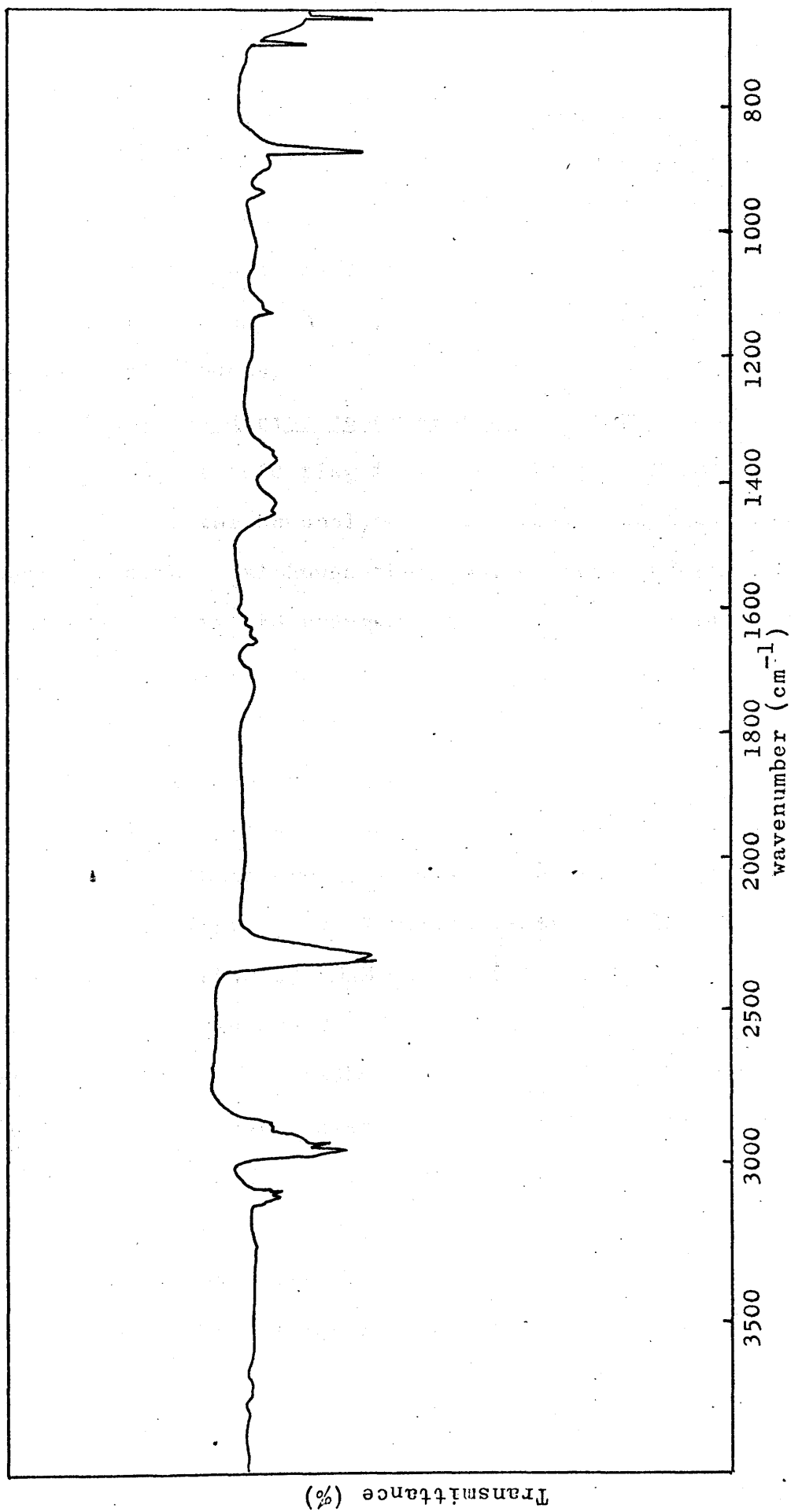


Fig. 7.9 IR spectrum gaseous volatiles from PMAA

of HNCO with NH_3 was not detected, white deposits were observed in TVA apparatus.

Quantitative analysis of non-condensables (CH_4, CO) was not attempted although these products appeared to be present in substantial amounts.

Structural changes during decomposition

IR spectra of cold ring fractions obtained from decomposition of the homopolymers have been discussed in the preceding section. Although they provide some information about the structural rearrangements which can take place during degradation, the best insight into the structural changes was obtained by heating the sample to a particular temperature and studying the modified polymer chain spectrum.

As the cyclization reaction in NH_4PMA will be compared with those of PMAM and PMAA, it will be convenient to discuss these polymers first. Fig. 7.10 illustrates the IR region of interest in (a) PMAM, (b) PMAM degraded to 310°C , (c) PMAA and (d) PMAA degraded to 225°C . Fig. 7.10(a) shows the carbonyl stretching vibration of PMAM to occur at 1655 cm^{-1} while the amide II band is clearly discernable at 1600 cm^{-1} . In the IR spectrum of PMAM degraded at 310°C (b), the major carbonyl absorption occurs at 1690 cm^{-1} and both amide I and amide II bands appear as shoulders upon the broad carbonyl absorption. Overlap of the residual amide carbonyl band with the imide carbonyl band places the maximum absorption just below 1700 cm^{-1} , normally observed in glutarimide and other cyclic imides.¹⁰⁴

Fig. 7.10(c) shows the appearance of new bands in PMAA degraded at 225°. These new bands at 1800 cm^{-1} and 1758 cm^{-1} are in close agreement with the twin peak observed by Grant and Grassie²⁵ in anhydropoly (methacrylic acid) and also with the value obtained for the corresponding six membered ring, glutaric anhydride.

Fig. 7.11 shows the region of primary interest in (a) NH_4PMA (b) NH_4PMA degraded at 220°C, (c) NH_4PMA degraded at 320°C. Fig. 7.11(a) shows $-\text{CO}_2^-$ stretching vibration to occur at 1550 cm^{-1} as in other metal salts of polymethacrylic acid, discussed in Chapter 3. Fig. 7.11(b) and (c) show that assignments similar to imidized PMAM and cyclized PMAA can be made in the modified NH_4PMA . Thus the above observation suggests that in NH_4PMA , the degradation proceeds by two routes, namely; loss of water and ammonia to result in cyclic imide structures and loss of ammonia alone to result in acid units with subsequent dehydration to cyclic anhydride.

Intramolecular cyclization in NH_4PMA seems to be the reasonable explanation as the relative viscosity of the polymer degraded at various temperatures (Fig. 7.12) was found to be decreasing a little instead of an increase as might be expected for crosslinking. The polymer became insoluble in water or any other common organic solvent after degradation to 175°C for an hour. This may have arisen because of an increase in the number of cyclized units or a few crosslinks which may have formed at that temperature.

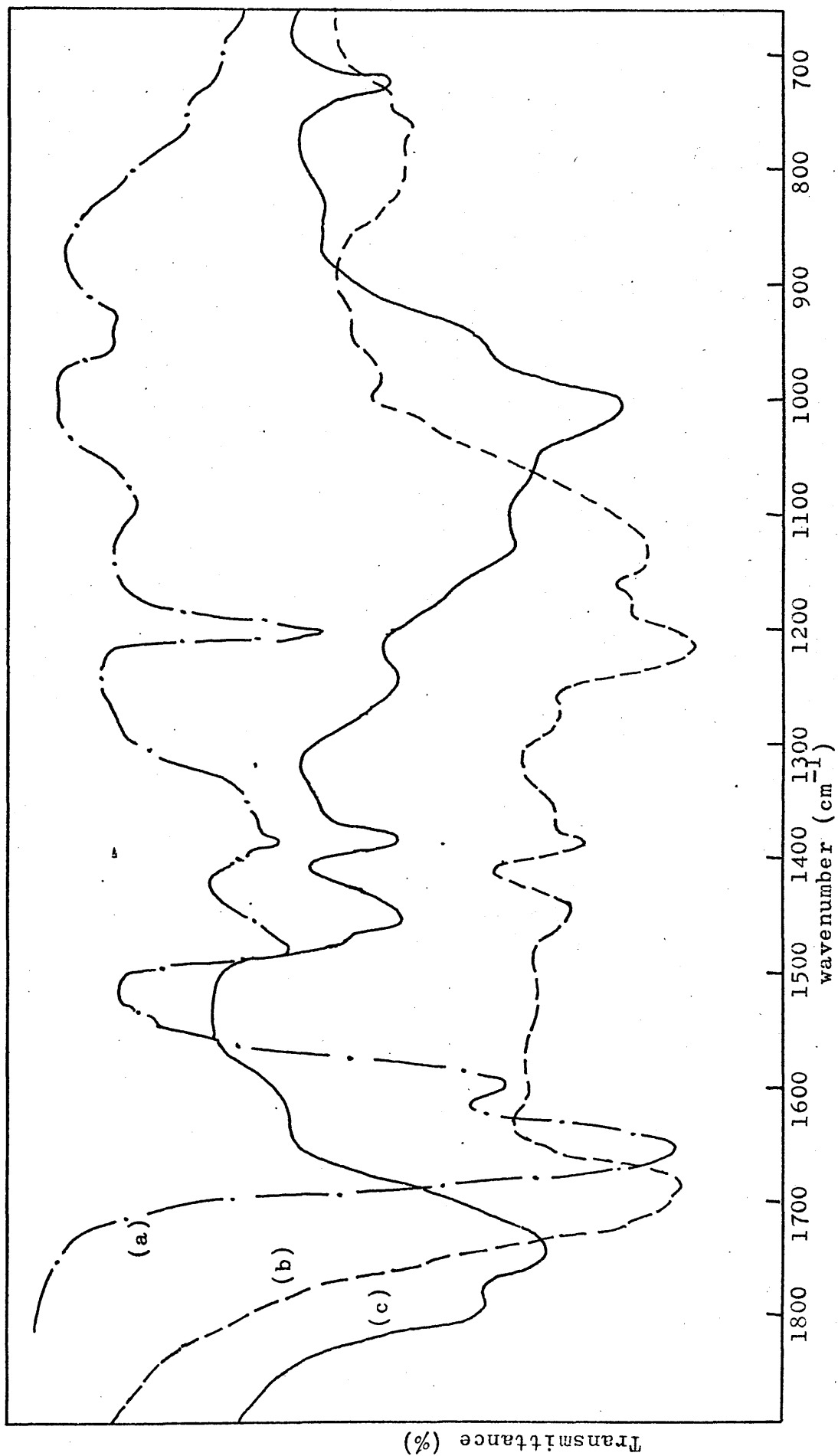


Fig. 7.10 IR absorption spectra of; (a) PMAM, (b) PMAM degraded to 310°C,

(c) PMAA degraded to 225°C

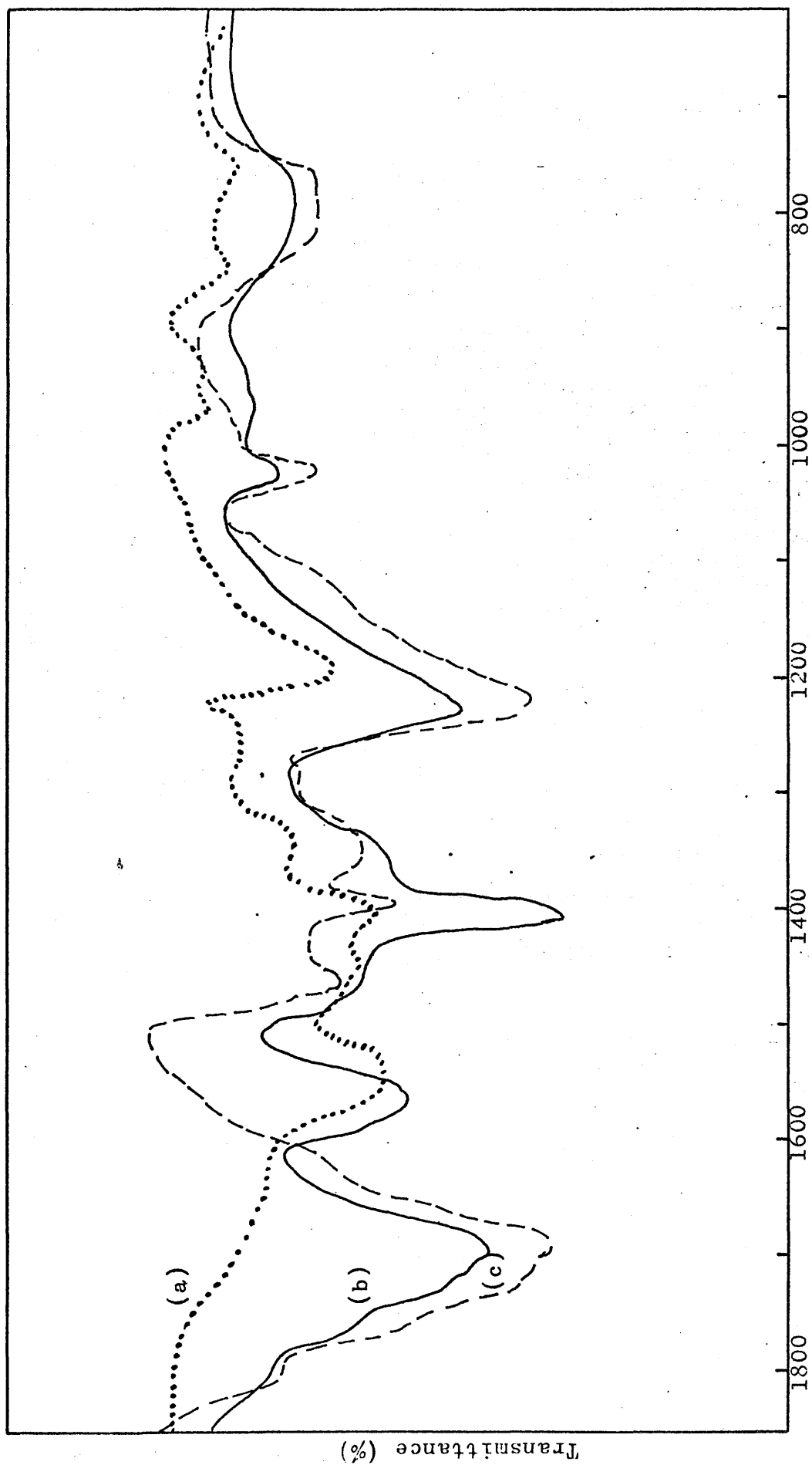


Fig. 7.11 IR absorption spectra of, (a) NH_4PMA , (b) NH_4PMA degraded to 220°C ,
(c) NH_4PMA degraded to 320°C .

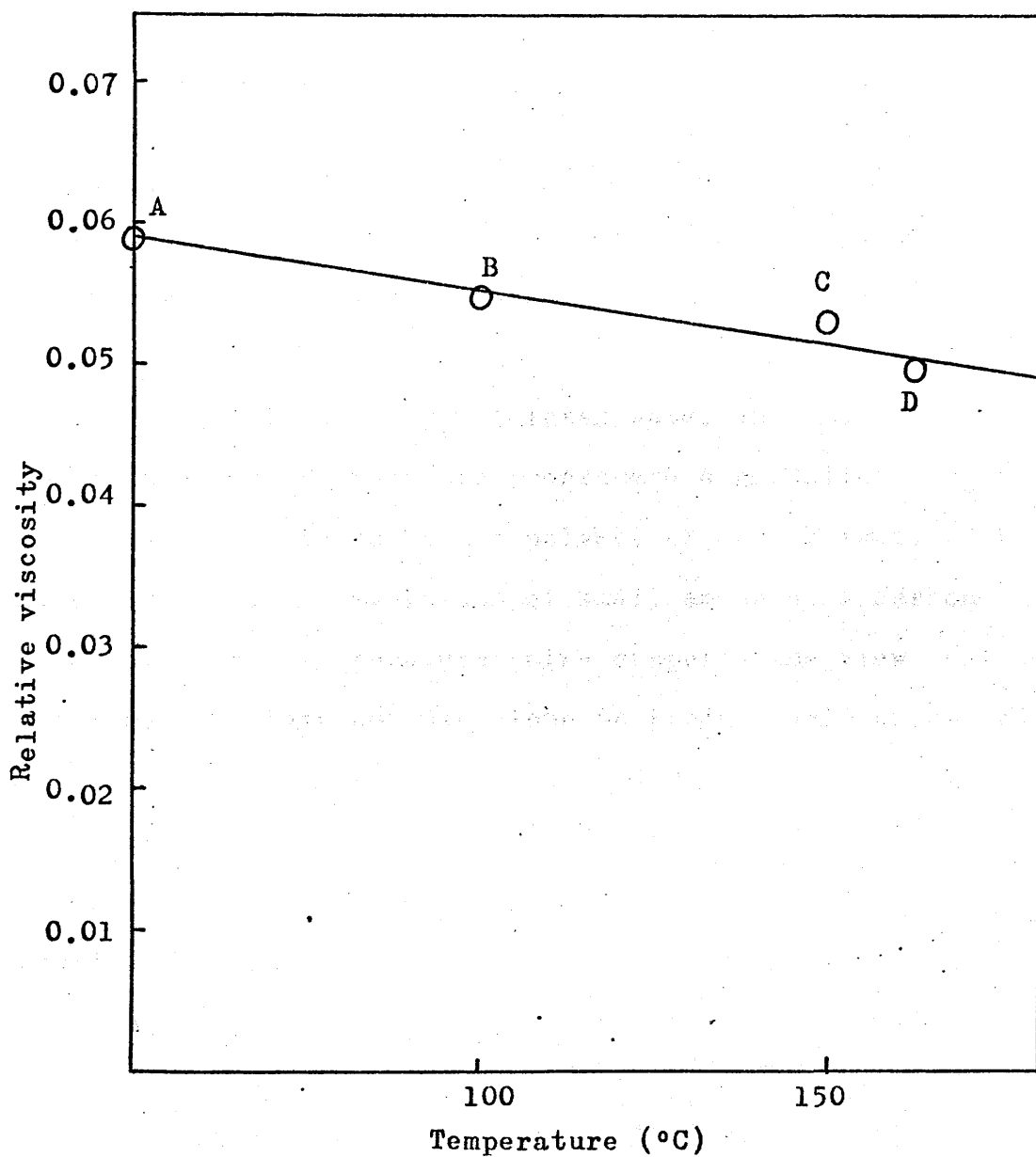


Fig. 7.12 Relative viscosities versus ammonium poly (methacrylate) isothermally degraded at various temperatures for one hour.

A = NH_4PMA undegraded

B = polymer degraded at 100°C

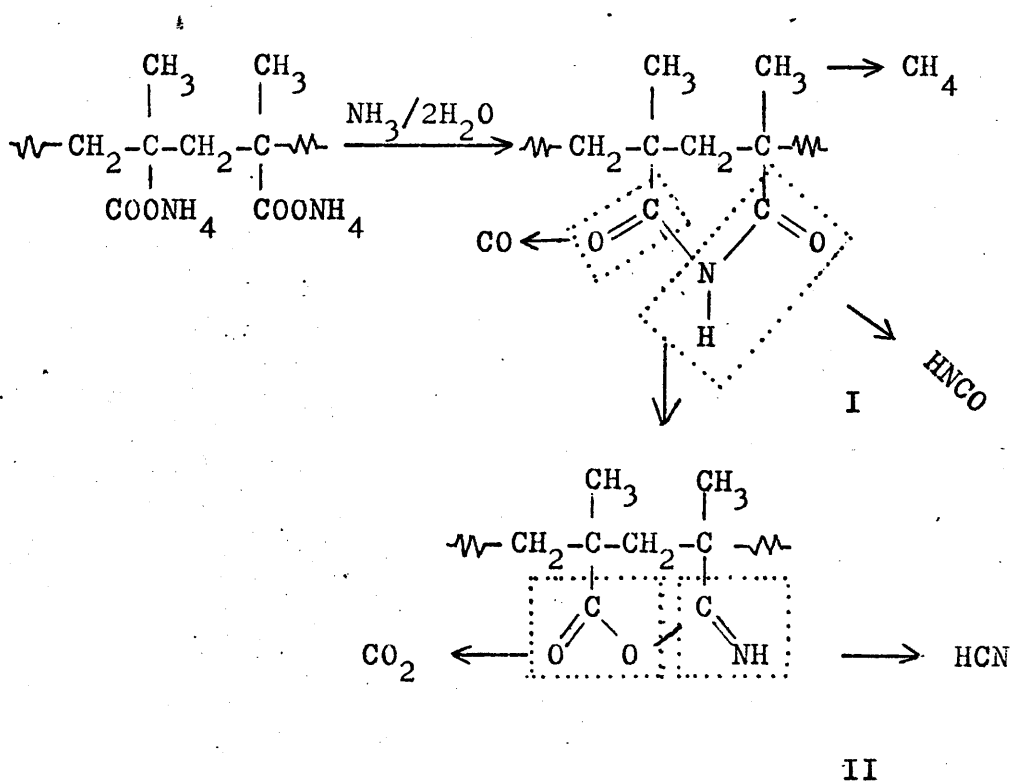
C = polymer degraded at 150°C

D = polymer degraded at 162°C

Proposed Mechanism

The basic features to be explained in the degradation of these homopolymers may conveniently be summarized at this point.

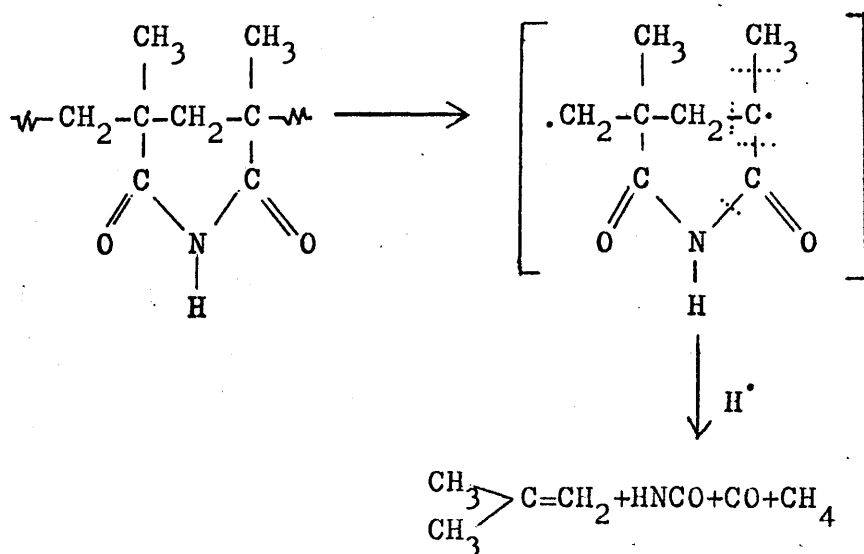
Ammonium polymethacrylate loses water and ammonia in the initial stages of temperature programmed degradation, to yield cyclic imide structures in the polymer chain. Formation of cyclic anhydride and evolution of small amounts of carbon dioxide at higher temperature also supports the view that the polymer may lose ammonia alone to produce acid units and then dehydrate to anhydride. Evolution of carbon dioxide can also be explained along with the formation of HCN in the following way, since imide structures are well known to isomerise:



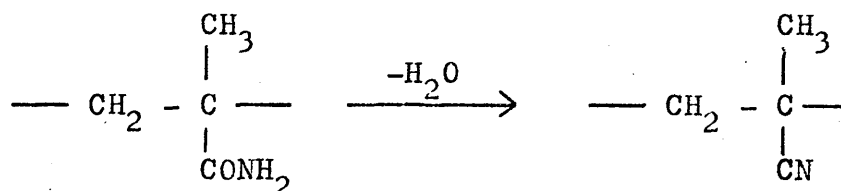
As HNCO appears in far larger quantities than carbon dioxide and HCN , it seems that equilibrium is in favour of the cyclic imide I. The structural changes during the degradation of NH_4PMA showed the formation of anhydride structures. These structures are known to give carbon dioxide as a major product. Thus carbon dioxide is formed by two routes, namely; isoimide and anhydride. Since carbon dioxide is evolved in small amounts, isoimide and anhydride formation may be minor reactions.

Polymethacrylamide shows that two outstanding features of decomposition can occur, namely intramolecular imidization and chain fragmentation to subsequent gaseous volatile products at higher temperature.

It has been noted in product analysis that PMAM gave 0.27% of isobutene and this may form by the decomposition of the back bone of imide structures;

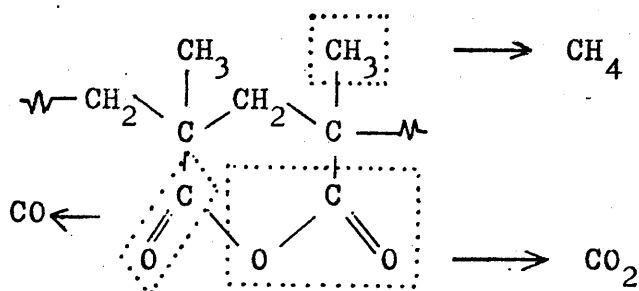


The unreacted amide units in PMAM and NH_4PMA can lose water; this may form methacrylonitrile obtained as a minor product from these homopolymers.

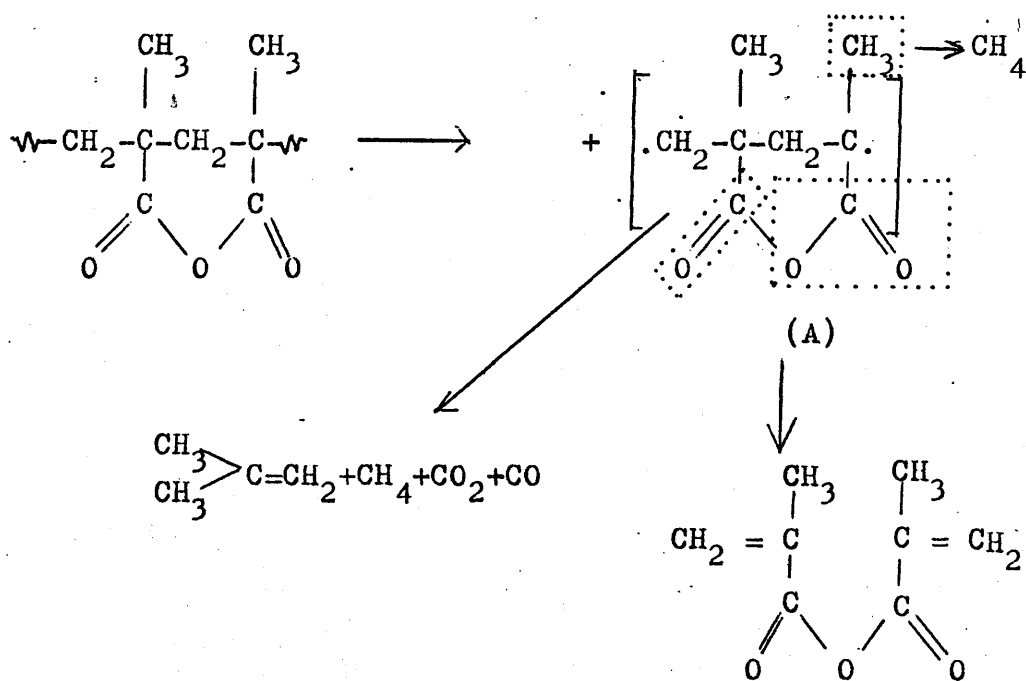


Small amounts of HCN and trace of carbon dioxide may again be formed from the isoimide structures, proposed in the case of NH_4PMA . Isocyanic acid was not observed as a degradation product in PMAM since it has been shown in product analysis (Fig. 7.8) that HNCO can be neutralized with ammonia if both are present in a system. This seems to be true as PMAM gave 0.8% of NH_3 during the final stage of degradation. PMAM has a coiled configuration, therefore it retains unreacted amide units throughout most of the degradation. These residual amide units become a further source of NH_3 and thus neutralize HNCO , which is formed by the decomposition of imide structures.

The formation of carbon monoxide, carbon dioxide and methane in the products of PMAA, has been explained by Jamieson and McNeill¹⁰⁵ who proposed that these may result from fragmentation of the anhydride ring structures.



They made no mention of isobutene, which was obtained as 1.37% of the total weight, in the present study. It seems that it may result from decarboxylation of the trapped monomer units between six membered anhydrides. The CRF of PMAA showed the presence of monomer anhydride and some long chain anhydride. Thus there must be a chain scission in the cyclized polymer.



Thus the radical species A either forms monomer or it may decompose to isobutene, methane, carbon monoxide and carbon dioxide. PMAM has a similar backbone and it gave a very small amount of isobutene compared to PMAA. Thus it seems that most of the isobutene produced, is formed from the decarboxylation of residual acid units. The production of isobutene from NH_4PMA can be explained in a similar fashion.

CHAPTER EIGHT

GENERAL CONCLUSIONS

The results of the present study may be summarised as follows:-

1. Metal salts of methacrylic acid were found to be thermally stable up to about 300°C. The alkali metal salts can be successfully polymerized in methanol solution under vacuum, using azodiisobutyronitrile as initiator.
2. Ammonium methacrylate can be polymerized in aqueous solution at elevated pH, using hydrogen peroxide as initiator.
3. The alkali metal salts of PMAA were found to decompose at much higher temperature than their parent homopolymer (PMAA). Evidence exists that depolymerization to monomer occurs accompanied by the formation of metal carbonate and cyclic ketones.
4. Decreasing amounts of cyclic ketones with increasing size of the metal ion suggests that syndiotacticity of alkali metal salts of PMAA increases with increased size of the metal ion. Similar evidence for the tacticity of divalent metal salts is also included.
5. Thermal degradation of divalent metal salts of PMAA further supports the mechanism proposed for the decomposition of alkali metal salts. The fact that divalent metal salts of

PMAA produce higher yields of cyclic ketones than the corresponding monovalent salts is regarded as an effect of the chemical nature of divalent metals.

6. Intramolecular cyclization seems to be an initial process of degradation in NH_4PMA and PMAM, before fragmentation to gaseous volatile products. The thermal degradation on mechanism of NH_4PMA is clearly seen to be the combination of processes evident in PMAM and PMAA decomposition.

7. Comparison of the thermal degradation of NH_4PMA , PMAM and PMAA is found to be feasible in determination of the role of single monomer units trapped between cyclic structures.

Suggestions for future work.

The molecular weights of the homopolymers were not determined in the present study because of the lengthy processes which would have been involved in their determination. However, molecular weight changes during degradation can provide valuable information. These changes can be determined by converting the salts to acids and then to esters whose molecular weight can be determined by osmometry.

The evolution of increased amounts of carbon dioxide with increased size of metal ion in alkali metal salts might be investigated by X-ray diffraction and electron microscopy in order to observe the possibility of formation of suboxide and superoxide.

The salt could be incorporated into a copolymer with co-monomer either MMA or AN to produce a polymer whose stability would be greater than that of PMMA or PAN respectively.

APPENDIX A

Sensitivity Factors Relative to N-Butyl Alcohol

Column: 13½% MEA and 6½% di-2-ethyl hexyl sebacate on chromosorb

Carrier gas: Helium

| Compound | Sensitivity factor(K) | Compound | Sensitivity factor(K) |
|----------------------------|-----------------------|---------------------------|-----------------------|
| 2.5 dimethylcyclopentanone | 1.4 | Methyl isopropyl ketone | 1.01 |
| 2.5 dimethylcyclopentanone | 1.28 | Methyl ethyl ketone | 1.1 |
| Methylcyclopentanone | 1.11 | Acetone | 0.9 |
| Cyclopentanone | 1.12 | Methacrolein | 1.3 |
| Diethyl ketone | 1.0 | Isobutyraldehyde | 0.85 |
| Di-isopropyl ketone | 1.14 | n-Butyraldehyde | 1.0 |
| Methyl n-propenyl ketone | 1.13 | Methyl isopropenyl ketone | 1.0 |

1. G.V. FERRY and S.J. GILL, J. Polym. Sci., 66, 999, (1962).
2. V. CRESCENZ et. al., Ric. Sci. Suppl., 29, 1424, (1959);
30, 1680, (1960); Chem. Abst., 54, 4109, (1959).
3. E.M. LOEBL and J.J. O'NEILL, Polym. Letters, 1, 27, (1963).
4. F.A. BOVEY, J. Polym. Sci., A1, 843, (1963).
5. E.M. LOEBL and J.J. O'NEILL, J. Polym. Sci., 45, 538, (1960).
6. G. SHROEDER, Makromol. Chem., 97, 232-40, (1966). Ger.
7. N. GRASSIE, "Chemistry of Polymer Degradation Processes",
Butterworths, London, (1956).
8. E.M. MONTROLL and R. SIMHA, J. Chem. Phys., 8, 721, (1940).
9. L.A. WALL, J. Res. Nat. Bur. Stand., 41, 315, (1948).
10. W.G. OAKS and R.B. RICHARDS, J. Chem. Soc., 2929, (1949).
11. A. VOTINOV, P. KOBKO and F. MOREI, J. Phys. Chem. (USSR),
16, 106, (1942).
12. N. GRASSIE and H.W. MELVILLE, Proc. Roy. Soc. (London),
A199, 24, (1949).
13. N. GRASSIE and H.W. MELVILLE, Proc. Roy. Soc. (London),
A199, 14, (1949).
14. N. GRASSIE and E. VANCE, Trans. Faraday Soc., 49, 184,
(1953).
15. S.L. MADORSKY, J. Polym. Sci., 11, 491, (1953).
16. S.L. MADORSKY, Thermal Degradation of Organic Polymer",
Interscience, New York, (1964).
17. N. GRASSIE, "Cleavage Reactions, Thermal Degradation", in
"Chemical Reactions of Polymers", E.M. FETTES (Ed.)
Interscience, New York.

18. G.C. MARKS, J.L. BENTON and C.M. THOMAS, S.C.I. Monograph, No. 26, London (1967), P.204.
19. D. DRUESDOW and C.F. GIBBS, Nat. Bur. Stand Circ., 525, 69, (1953).
20. R.R. STROMBERG, S. STRAUS and B.G. ACHHAMMER, J. Polym. Sci., 35, 355, (1959).
21. E.J. ARLMAN, J. Polym. Sci., 12, 543, (1954).
22. N. GRASSIE, Trans. Faraday Soc., 48, 379, (1952).
23. J.P.W. HOUTMAN, J.V. STEENIS and P.M. HEERTJES, Rec. Trav. Chim., 65, 781, (1946).
24. A. MACCOLL, J. Chem. Soc., 3398, (1958).
25. D.H. GRANT and N. GRASSIE, Polymer, 1, 445, (1960).
26. N. GRASSIE and J.N. HAY, J. Polym. Sci., 56, 189, (1962).
27. N. GRASSIE and J.N. HAY, S.C.I. Monograph No. 13 (1961). London.
28. D.H. GRANT and N. GRASSIE, Polymer 1, 125, (1960).
29. S.E. BRESLER, M.M. KOTON, A.T. OSMINSKAI, A.G. POPOV and M.N. SAVILSKAIA, Polym. Sci. (USSR), 1, 393, (1960).
30. D. DOLLIMORE and G.G. HEAL, Carbon, 5, 65, (1967).
31. N. GRASSIE and I.C. McNEILL, J. Polym. Sci., 30, 37, (1958).
32. N. GRASSIE and I.C. McNEILL, J. Polym. Sci., 27, 207, (1958).
33. A. MACCOLL, Chem. Rev., 69, 33, (1969).
34. N.L. ZUTTY and F. WELCH, J. Polym. Sci. A, 2289, (1963).
35. Y. KIKUCHI and K. YAMAOKA, J. Science, The Hiroshima Univ. Ser. A, Vol 21, No.2, (1957).
36. R.P. HOPKINS, Ind. Eng. Chem., 47, 2258, (1955).

37. S. FURUKAWA, M. SHINKICHI and N. KIYOSHI, Chiba Daigaku Kogakubu Kenkyu Kokoku, 14 (25), 39-46, (1963).
38. S. FURUKAWA et. al., J. Fac. Eng. Chiba University, 17, 33, (1966).
39. S. FURUKAWA and K. NARUCHI, Chiba Daigaku Kogakubu Kenkyu Hokoku, 16 No.29, 83, (1965).
40. S. FURUKAWA and K. NARUCHI, Ibid., 16 No.29, 92, (1965).
41. I.C. McNEILL, J. Polym. Sci., A4, 2479, (1966).
42. I.C. McNEILL, Europ. Polym. J., 3, 409 (1967).
43. I.C. McNEILL and D. NEILL, Thermal Analysis, 353; R.F. Schwenker and P.D. Garn (Eds.), Academic Press, New York (1969).
44. I.C. McNEILL, "Thermal Analysis", 417, R.F. Schwenker and P.D. Garn (Eds.), Academic Press, New York, (1969).
45. I.C. McNEILL, Europ. Polym. J., 6, 373, (1970).
46. I.C. McNEILL and D. NEILL, J. Thermal Analysis, 1, 389, (1969).
47. G. BRAUER, "Hand-book of Preparative Inorganic Chemistry", (2nd Ed.), Vol. 1, 658-659, (1963).
48. C.W. SMITH and D.G. NORTON, Org. Syn. Coll. Vol 4, 348, (1963)
49. H. STAUDINGER and H.W. KLEVER, Ber., 39, 968, (1906).
50. C.D. HURD and M.F. DULL, J. Am. Chem. Soc., 54, 2432, (1932).
51. H. STAUDINGER, Helv. Chim. Acta, 8, 306, (1925).
52. E. OTT, Ann., 401, 159, (1913).
53. W.E. HANFORD and J.C. SAUER, Org. Reactions, 3, 136 (1949).
54. M. MUNGO and M. BORNEGO, Chim. Ind.(Milan), 45, 1216, (1963); 46, 5, (1964).

55. W.H. FLETCHER and W.B. BARISH, *Spectrochimica Acta.*, 21, 1647-61, (1965).
56. H. MORAWETZ and I.D. RUBIN, *J. Polym. Sci.*, 57, 669-86, (1962).
57. B.M.J. BOWDEN, J.H. O'DONELL and R.D. SOTHMAN, *Diemakromol. Chemies.*, 122, 186-195, (1969), (Nr.2950).
58. J.H. O'DONELL and R.D. SOTHMAN., *J. Polym. Sci. Part A-1*, 6, 1073-1086, (1968).
59. J.B. LANDO, H. MORAWETZ, *J. Polym. Sci. Part C*, 4, 789-803, (1964).
60. KALCHALSKY and BLUER, *Trans. Faraday. Soc.*, 47, 1360, (1951).
61. KALCHALSKY and SPITNIK, *J. Polym. Sci.*, 2, 432, (1947).
62. KALCHALSKY, KUNZLE and KOHN, *J. Polym. Sci.*, 5, 283, (1950).
63. KALCHALSKY and GILUS, *Rec. Trav. Chim.*, 68, 879, (1949).
64. KALCHALSKY and EISENBERG, *J. Polym. Sci.*, 6, 145, (1951).
65. G. BLUER, *Trans. Faraday. Soc.*, 56, 606-12, (1960).
66. A.I. VOGEL, "Quantitative Inorganic Analysis", 3rd Ed., Longmans, London, (1961).
67. F.A. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry", (2nd Ed.), Interscience, London.
68. S.A. RICE, M. NAGASAWA and H. MORAWETZ, "Polyelectrolyte Solutions", Academic Press, London, p.432, (1961).
69. H. MORAWETZ, A.M. KOTLIAR and H. MARK, *J. Phy. Chem.*, 58, 19, (1954).
70. A.M. KOTLIAR and H. MORAWETZ, *J. Chem. Soc.*, 77, 3692, (1955).

71. F.T. WALL and W.J. GILL, *J. Phy. Chem.*, 58, 1128, (1954).
72. H.P. GREGOR, L.B. LUTTINGER and E.M. LOEBL, *J. Phy. Chem.*, 59, 34, (1955).
73. S. FRONAEUS, *Acta. Chem. Scand.*, 5, 859, (1951).
74. M. MANDLE and J.C. LEYTE, *J. Polym. Sci. Part A*, 2, 2283-99, (1964).
75. L.A. NOLL and S.J. GILL, *J. Phy. Chem.*, 67, 498, (1963).
76. J.C. LEYTE, L.H. ZUIDERWEG and J.H. VLEDDER, *Spectrochimica Acta.*, 23A, 1397-1407, (1967).
77. N. GRASSIE and H.W. MELVILLE, *Discussions Faraday Soc.*, 2, 378, (1947).
78. N. GRASSIE and J.R. MacCALLUM, *J. Polym. Sci.*, 2A, 983, (1964).
79. H. SCHULTZ and J. SICKELS, *J. Chem. Edu.*, 38, 300, (1961).
80. G.G. CAMERON and D.R. KANE, *J. Polym. Sci.*, B2, 693, (1964).
81. ARDAGH, BARBOUR, McCLELLAN and McBRIDE, *Ind. Eng. Chem.*, 16, 1133, (1924).
82. N.C. COOK, A.L. MILLER and F.C. WHITMORE, *J. Am. Chem. Soc.*, 72, 2732, (1950).
83. R.I. REED and J.J. O'NEILL (unpublished observations).
84. J. BELL and R.I. REED, *J. Chem. Soc.*, 1383, (1952).
85. ROJAN and SCHULTEN, *Ber.*, 59, 499, (1926).
86. KRONIG, *Z. Agnew Chem.*, 37, 667, (1924).
87. R.C. WEAST, "Handbook of Chemistry and Physics", 55th Ed. (1974-75).

88. S. FURUKAWA, S. MIYAZAWA and K. NARUCHI, Chiba Daigaku Kogakubu Kenkyu Kokoku, 14(26), 116-223, (1963).
89. S. FURUKAWA, K. NARUCHI and N. KUMAKAWA, Chiba Daigaku Kogakubu Kenkyu Kokoku, 17(32), 1-7, (1966).
90. E. BAMBERGER, Chem. Ber; 43; 43, 3517, (1910).
91. G. BLANC, Bull. Soc. Chim. (Belges), 4 series, 3, 778, (1908).
92. M.M. SHEMYAKIN and E.M. BAMBAS, Zh. Obshch. Khim., 18, 629, (1948).
93. H. KOCH and E. LEIBNITZ, Periodica Polytech., 5, 139, (1961).
94. O. NEUNHOEFFER and O. PASCHKE, Chem. Ber., 72, 919, (1939).
95. D. DOLLIMORE, D.L. GRIFFITHS, and D. NICHOLSON, J. Chem. Soc., 2617, (1963).
96. H. STUDINGER, Helv. Chim; Acta, 12, 1107, (1929).
97. K. CRAWELS and G. SMETS, Bull. Chem. Soc., Belges, 59, 182, (1950).
98. H.C. HAAS, R.L. McDONALD, J. Polym. Sci., A1, 3583, (1971).
99. C.S. MARVEL and C.L. LEVESQUE, J. Am. Chem. Soc., 60, 280, (1938).
100. C.S. MARVEL and C.E. DENOON, J. Am. Chem. Soc., 60, 1045, (1938).
101. C.S. MARVEL, J.H. SAMPLE and M.F. ROY, J. Am. Chem.Soc., 61, 3241, (1939).
102. T. ALFREY, Jr., H.C. HAAS and C.W. LEWIS, J. Am. Chem. Soc., 73, 2851, (1951).

103. N. GRASSIE and J.N. SAMSON (unpublished observations).
104. C.J. POUCHERT, Aldrich Library of IR Spectra, Aldrich Chem. Co., (1970).
105. A. JAMIESON and I.C. McNEILL, Europ. Polym. J., 10, 217-225, (1970).
106. G.F. PREGAGLIA and M. BINAGHI, Macromolecular Syntheses, Vol. 3, 154-160, (1968).

